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# CHEMICAL REACTIONS

## THEIR THEORY AND MECHANISM

Zuitman

BY

K. GEORGE FALK, PH.D.

HARRIMAN RESEARCH LABORATORY,
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# PREFACE

THE central idea of this book is the development of a general theory of reactions which will include both inorganic and organic reactions. The fundamental view upon which this theory is based is the "addition" theory according to which when two or more substances react a primary addition is the first step. This theory is not new. It has been used in more or less isolated cases for a number of reactions and may have been suggested as of general applicability. As far as the writer is aware, however, this is the first time that it is published in an extended form with modern conceptions of chemical structures, which themselves rest upon the development of valence views.

The modern interest in valence appears to have started in 1899 when Thiele published his paper on partial valence. Some years later, 1904, J. J. Thomson suggested the basic ideas of the electron conception of valence, but applied these to very few cases. From that time on, the electron conception of valence occupied the minds of a number of chemists who attempted its application as shown in sporadic publications. Professor Nelson and the writer believe that they were the first, dating from 1909 on, to publish extended applications of the electron conception of valence to organic as well as to inorganic compounds and reactions, and to develop certain lines of chemical theory from this point of view. In the development of these views, they travelled over a certain course of chemical thinking. Unquestionably, others have followed the same or similar lines of thought and reached similar conclusions. Among those who have published along these lines may be mentioned H. S. Fry, W. A. Noyes, J. Stieglitz, L. Jones, G. N. Lewis,

R. F. Brunel, W. C. Bray and G. E. Branch, S. Dushman, J. Stark, H. Kauffmann, and a number of others. No attempt will be made to give a historical review of the problem or to determine who is responsible for any particular part of the theory. That it was possible for certain workers to publish before others does not negative the fact that such theoretical views may have been taught and used in planning experimental work by either group long before their publication.

For practical reasons, it was not possible for Professor Nelson and the writer to add to the experimental data from the newer point of view, but it seemed at the time as if sufficient facts were recorded in the literature to permit of a conclusive test of the theory.

The electron conception of valence has now apparently been widely accepted. At the same time, a number of chemists still speak of polar and non-polar valences. To the writer, no useful purpose is served by such a distinction.

As stated, chemical reactions form the keynote of this book. The first three chapters are preliminary in the sense that they treat of the underlying theoretical conceptions used in the later chapters. Certain parts of Werner's theoretical views are used. At present, these appear to offer the only explanation which is at all satisfactory for what have been termed at various times "molecular" compounds. In recent years, G. N. Lewis and I. Langmuir have developed certain conceptions of molecular structures from the point of view of electron distribution. These conceptions are of the utmost importance and indicate new methods of formulation. To apply them to the consideration of chemical reactions appears to be somewhat premature. At least, it appears to the writer that for him to attempt it would be so. Since their views are not used here and since this is in no way a historical treatise, they have not been given in detail. On the other hand, it is believed that enough of

the general theoretical side has been given to permit any one interested to follow intelligently any further developments of structural chemical theory.

Questions of stereochemistry have not been included. It would appear that spatial chemistry is entering upon a new phase. The experimental and theoretical work on the arrangements of atoms in crystals as exemplified in the publications of the Braggs and of others, points to an entirely new conception of stereochemistry, while at the same time stereochemical explanations, such as steric hindrance, which have been accepted heretofore, are being superseded by explanations based upon different relationships.

A number of new points of view and explanations are advanced here. Many of these have been presented by Professor Nelson to his students at Columbia University during the past years. Whatever value this book may possess is due in a large measure to him, both in the development of the views and in the collection of material. Among others who have aided in various ways in the development of the views leading up to the preparation of this book and to whom thanks are due are Professors G. B. Pegram and H. T. Beans, of Columbia University, and Dr. Marston L. Hamlin.

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# CONTENTS


CHAPTER I.

PAGE

INTRODUCTION; VALENCE ..... 1

CHAPTER II.

VALENCE (CONTINUED); CO-ORDINATION NUMBER .... 21

CHAPTER III.

ACIDS AND BASES ..... 41

CHAPTER IV.

CATALYSIS ..... 60

CHAPTER V.

CHEMICAL REACTIONS; GENERAL CONSIDERATIONS ... 76

CHAPTER VI.

SOME CHEMICAL REACTIONS ..... 94

CHAPTER VII.

SOME CHEMICAL REACTIONS (CONTINUED) ..... 120

CHAPTER VIII.

OLEFINS AND THEIR REACTION PRODUCTS ..... 135

CHAPTER IX.

OXIDATION-REDUCTION ..... 166

CHAPTER X.

SOME OXIDATION-REDUCTION REACTIONS ..... 190

# CHEMICAL REACTIONS

## CHAPTER I.

### INTRODUCTION; VALENCE.

In order to classify chemical reactions so that it will be possible to obtain a knowledge of the relations involved when chemical changes take place without considering each chemical reaction as an individual unrelated to any other, certain general theories must be established. These theories have been developed gradually as the number and kinds of chemical reactions increased. They are not complete enough yet to account for all possible changes but they serve a useful purpose and make possible the study of relationships which would be obscure without them. The general principles upon which the theories of the mechanism of chemical reactions depend and which will be used here include I. The atomic and molecular theories; II. Valence, including atomic valence and the electron conception of valence, and co-ordination number; III. Reaction velocity, especially as controlled by the physical conditions and by the law of mass action.

These principles indicate the lines which will be followed in the correlation of chemical reactions. Thermodynamic relations will be considered only secondarily. Molecular and atomic chemistry, and in general, kinetic relationships will be the keynote of the explanations advanced. The atomic and molecular theories together with valence conceptions form the foundations. Reaction velocities are the important features in considering chemical reactions and the course these may take under given conditions. It is impossible to treat of a reaction velocity without treating

at the same time the velocity of the reaction in the opposit direction, or in other words, the equilibrium of the reactio Equilibria are therefore arrived at from the kinetic an molecular standpoints. This is as far as the theoretica side of the treatment in this book will go. It may b pointed out that the thermodynamic treatment reaches th same point from the opposite direction. From the energ relationships, deduced from the laws of thermodynamics the equilibria relationships of chemical reactions are arrive at. One of the future problems of thermodynamic chem istry is the development of reaction velocity relationship from the equilibria concepts.

The reader of this book is supposed to have completed a course in general inorganic and organic chemistry from the modern point of view. The relations of chemistry are supposed to have been studied in such a way that the elementary facts and phenomena are accurately described, and the theories which develop from these facts and phenomena applied and used in a rational manner. Such a study would include a portion of the subject matter of what is very often taken up at present under "physical chemistry."

The atomic theory is based upon the laws of definite and multiple proportions. Exact analyses of many substances have shown that the constituent elements of these substances are combined in such quantities that definite amounts or their multiples are always combined with each other. The atomic theory gives a definite and simple theory to account for this. The molecular theory is based upon the existence of certain quantitative relationships between the chemical compositions of substances and their relative volumes in gas form or osmotic pressures in dilute solutions. These theories were based upon quantitative experimental data and accounted for them satisfactorily. In recent years the existence of atoms and molecules has

been demonstrated experimentally so that no question remains as to their existance. The reader is referred to the book entitled "The Atom" by J. Perrin for an account of his work.

The terms equivalent or combining weight and formula weight have been used in place of atoms and molecules as not involving the theories of atoms and molecules. While these terms may have been useful at a time when the existence of atoms and molecules were to some extent hypothetical, the proof of their existence in recent years has made the use of such terms unnecessary.

Following the atomic and molecular theories, the study of the chemical compositions of substances led to the doctrine of valence or saturation capacity. Each atom is considered to be capable of combining with a definite number of atoms of its own kind or a different kind. The arrangement of the elements in the Periodic System of Mendeléeff brings out clearly these valence numbers. The introduction of dots and dashes in chemical formulas to represent valence linkings forms a convenient method of representation.

Sometimes confusion has been caused by taking valence linkings to represent some form of combining power or stability. This question must be made clear and the meaning of valence defined carefully for a proper understanding of the questions to be taken up. In order to do this, chemical energy will be taken up for a moment and the relation between it and valence described.

For some purposes, it has been considered that energy might be assumed to be the product of two factors, an "intensity" factor and a "capacity" factor. For example, in mechanical work or energy, in which the work is taken to be equal to the product of force into distance, the force would be the intensity factor and the distance the capacity factor. This division of energy into factors is entirely

arbitrary. It serves a useful purpose in certain cases, bu its limitations must be remembered. The intensity an capacity factors of mechanical energy need bear no relatio except in name, to the intensity and capacity factors o electrical energy or of chemical energy or of any other for of energy. For each form of energy a different divisio may be made. This can be shown most directly by express ing the two factors of some of the different forms of energy in terms of the C.G.S. system of length ($L$), mass ($M$), an time ($T$) units. The dimensions of energy are always give by the expression $ML^2T^{-2}$. In energy considered as me chanical work, force may be called the intensity factor an is given by the product of mass times acceleration or $MLT^{-2}$ and the displacement the capacity factor equal to $L$. In electrical energy, for an electrostatic current, the electro motive force may be called the intensity factor and is given by the expression $M^{1/2}L^{1/2}T^{-1}$, and the electricity or charge or coulombs the capacity factor and given by the expression $M^{1/2}L^{1\ 1/2}T^{-1}$. These two sets of factors show the usual way of viewing the intensity and capacity factors of these two forms of energy. For chemical energy, still another way of viewing the possible energy relations is customary. Here, the intensity factor may be considered to be given by the change of free energy of the reaction under certain definite conditions to be formulated presently. This is the chemical affinity, and the units in which it is expressed given by $ML^2T^{-2}$. Obviously then, the capacity factor of chemical energy would be a number. This numerical capacity corresponds to what is known as valence.

This brief statement required further explanation, however. If the change in free energy is referred to the combination taking place between equivalent weights of chemical substances, that is to say, between the unit weights of chemical combination, then, when considering molecules or formula weights, the numbers of equivalents taking

part would indicate the capacity factor or valence. Valence is therefore represented as a number and the product of change in free energy per equivalent and valence represents the change in free energy in the formation of the substance in the molecular state. In ferrous chloride, for example, the free energy or chemical affinity of the two chlorine atoms in combination with the iron may be assumed to be the same; in ferric chloride, similarly, that of each of the three chlorine atoms may be assumed to be equal, but not necessarily the same as for the chlorine atoms in ferrous chloride. The difficulty, if not impossibility of determining the free energy change when two atoms of a more complex molecule combine, makes it necessary in practice to speak only of the change in free energy in the formation of a compound and not of the separate combinations between pairs of atoms in the compound.

Keeping in mind the significance of the terms intensity and capacity factors, they will now be used in discussing chemical energy as they form a convenient method for presenting certain definite relationships. The chemical energy contained in a given compound having a definite molecular formula involves the number of atoms in the molecule and the affinity with which these atoms are combined with each other. The chemical affinity involved in a compound is a definite quantity. It is given numerically as the value of the affinity of that compound compared to the value of the affinity of the substances from which it is formed. That is to say, the chemical affinity of a compound is given as a difference, not as an absolute value. It may be measured in any of the ordinary units of energy, and represents the external work which may be obtained when the substance is formed from its component parts by a reversible isothermal reaction. This external work is generally known as the change in free energy in the formation of the compound and is the true measure of the change

in the chemical affinity. The actual measurements of these values may be carried out in several ways. A direct method involves the electromotive force measurements of a reversible cell under definite conditions. A more general method is the determination of the equilibrium constants of definite reactions. At the present time very few organic reactions are available for the former method, while for the latter, the accurate determinations of a large number of equilibria in organic reactions have not been carried out. There are, consequently, comparatively few data at hand to enable the exact relative thermodynamic stabilities of organic compounds to be calculated. It is very desirable that such determinations be made, as they represent one of the most important problems in chemistry at the present time. Such values would give a true measure of the relative stabilities of compounds, or the magnitude of the chemical affinities. Many organic chemists have been in the habit of speaking of the stability of a compound when the rate at which the compound reacted was meant. Reaction velocities bear no simple relation to the stability or affinity, and deductions with regard to the affinity with which two atoms are combined, simply on the basis of the rate with which they react with other substances, are wrong in principle and fact.

The terms upon which the intensity factor of chemical energy or the chemical affinity depend may be indicated as follows: Every reaction is (thermodynamically) reversible. The greater the affinity which causes two substances to combine or react, the greater will be the proportion or amounts of the products formed, and the more difficult will it be to decompose the products. The chemical affinity will consequently be greater, the more the equilibrium lies in the direction of the formation of the products; or, in other words, the value of the chemical affinity is connected with, or may be calculated from some function of the

equilibrium constant. Van't Hoff, in 1883, showed this function to be given by the equation

$$(1) \qquad A = RT \log_e K - RT \log_e \frac{C_{M'}^{n'_{a'}} C_{N'}^{n'_{b'}} \ldots}{C_M^{n_a} C_N^{n_b} \ldots}.$$

for a chemical reaction represented by the equation

$$(2) \qquad n_a M + n_b N + \ldots = n'_{a'} M' + n'_{b'} N' + \ldots,$$

in which $A$ represents the change in free energy or the chemical affinity of the reaction (2); $R$, the gas constant; $T$, the absolute temperature at which the reaction takes place; $K$, the equilibrium constant of the reaction represented by equation (2); and the different values of $C$ in the second term of the right-hand side of equation (1) the concentrations of the reacting substances of equation (2). If these concentrations are chosen as equal to unity, the chemical affinity is found to be

$$(3) \qquad A = RT \log_e K.$$

The relation between the equilibrium constant, $K$, of a reaction, and the heat, of the reaction at constant volume $Q$, both at the absolute temperature $T$, was shown by Van't Hoff to be

$$(4) \qquad \frac{d \log_e K}{dT} = - \frac{Q}{RT^2}.$$

The following equation, (5), is known as the Gibbs-Helmholtz equation.

$$(5) \qquad A = Q + T \frac{dA}{dT}.$$

This shows the relation between the change in free energy, or the chemical affinity of a reaction, the heat of reaction at constant volume, the absolute temperature at which the reaction proceeds, and the temperature coefficient of the chemical affinity, $dA/dT$, of the reaction. These three

equations are fundamental for the relations between the chemical affinity of a reaction and other physical and chemical quantities.

The last equation shows that only if $T = 0$ or if $dA/dT = 0$ is the heat of reaction equal to the chemical affinity. The equality of these two is therefore only a special case, and as $T$ increases, they are likely to diverge more and more. Whether the heat of reaction is greater or less than the chemical affinity will depend upon whether the change in the chemical affinity with the temperature is negative or positive. In equation (5) the electromotive force of a reversible cell per gram-equivalent of substance transformed (since one faraday of electricity is associated with one gram equivalent of substance) may be substituted for $A$, since it is a measure of the change of free energy of the chemical reaction taking place in such a cell.

The capacity factor of chemical energy may be considered to be valence. Valence is a number, and is a distinct factor not involving chemical affinity. For reasons which have already been given, the chemical affinities of organic compounds have been determined only in isolated cases. On the other hand, valence has been a valuable aid in classifying the compounds of organic chemistry, so that it is the latter which has been used to the greater extent in that field. At the same time another reason for this may be given. The change in free energy, or the thermodynamic stability, while of the greatest importance, has nothing to do with the time factor. That is to say, it gives the stability of a compound when equilibrium has been reached. Now the element carbon often shows great inertia or chemical resistance in many of its compounds and reactions. The velocity with which it enters into reactions is often very small even though the free energy involved in the chemical change is very great. As a result, compounds of carbon are known which have no thermodynamic right to exist,

that is to say, if equilibrium were attained, none or only infinitesimal amounts of the substances would be present. The rate of reaction is so small, however, that equilibrium ordinarily is not attained, and therefore organic chemistry has very often to deal with these (thermodynamically) unstable substances. While, therefore, undoubtedly, the affinity relationships of organic compounds will ultimately be of predominant importance, until more is known of these, valence, which is not affected by the time factor in this way, has had to serve as the classifying principle. But in using valence in this way it is not permissible to introduce exact measures of the comparative stabilities as has been attempted so often, as already pointed out. All that can be done as a result of the comparative study of large numbers of compounds is to say which would probably exist under ordinary conditions and whether some would react more rapidly than others. These qualitative factors do not give any information concerning the real quantitative measures of relative stability.

A single linking between two atoms gives no information as to the stability of the union between these atoms. A double linking between two atoms cannot give any more information with regard to the stability of the union. Qualitatively, it has been found that the rate of reaction for compounds containing double linkings is greater in some ways than the rate for compounds containing single linkings, and that with certain reagents, decomposition at the double linking occurs more rapidly than at other parts of the molecule, but this is manifestly different from a discussion of true stabilities of compounds. The double linking in the ordinary language signifies two units of valence just as the single linking denotes one unit of valence, and in this sense, the only permissible one, the representation of a double linking by two lines or dashes is a correct picture of the union when one line is used for the single linking.

These valence views may now be carried further and the later conceptions involving the electrons and the electron conception of valence described. These developments did not take place suddenly but occurred gradually as new experimental work showed that the older views were not sufficient to include all the facts known. For instance, oxides are at times spoken of as acid oxides and basic oxides. Electrolytic studies on the decomposition of salts and other substances in solution indicate a real difference between the two parts of the molecules. The distinction may be carried further and acid-forming elements and base-forming elements designated, as brought out, for instance, by the oxides of the elements of the different groups in the Periodic System. The names non-metals and metals may be taken to be practically synonymous with acid-forming and base-forming elements, and finally these may be used interchangeably with electronegative and electropositive elements. This development of terminology leads to the following definition or description of valence: The valence of an element is equal to the number of equivalents of the acidic or of the basic constituents combined with or associated with one formula weight of that element. Arrhenius's theory of ionization has shown that certain of the atoms or groups actually do carry electric charges, and has fixed the terms electropositive and electronegative as having a readily demonstrable existence with these substances.

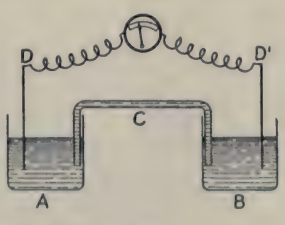
J. J. Thomson, in 1904, put forward as a possible development a new view of valence. Instead of quoting the brief presentation given by him, an attempt will be made to develop the subject more completely. If a solution of ferrous chloride is placed in beaker *A*, and a solution of potassium permanganate in beaker *B*, the two solutions connected by a salt bridge *C* containing a solution of some neutral salt dipping into both solutions, and by a wire with

a galvanometer in circuit connecting the two electrodes $D$ and $D'$ which dip into the solutions, it will be noticed that a positive current will flow in the direction $B$ to $A$ in the wire. If the contents of beaker $A$ be examined now, it will be seen that the iron has been oxidized to the ferric form. If the amount of positive electricity flowing through the circuit from $B$ to $A$ were measured and the amount of ferrous iron changed into ferric iron were also measured, it would be found that for every formula weight, or mol, of ferrous iron changed into ferric iron, 96,500 coulombs of electricity had passed through the circuit. Therefore it may be said that one mol of ferrous iron differs from one mol of ferric iron by 96,500 coulombs. In this way it may be brought out that

One mol of iron = 56 grams of iron.
" " " ferrous iron = 56 grams of iron—$2 \times 96{,}500$ coulombs negative electricity.
" " " ferric iron = 56 grams of iron—$3 \times 96{,}500$ coulombs negative electricity.

From these values it is evident that the amount of positive electricity associated with the mol of iron corresponds to the number of mols of atomic chlorine that the mol of iron can hold in chemical union, or, in other words, there is a definite relation between the amount of electricity and the valence of the iron.

If, instead of a solution of ferrous chloride, an alkaline solution of formaldehyde is placed in beaker $A$, it will be found that again a positive current will flow from $B$ to $A$, in the wire, and if the constants of beaker $A$ are examined, it will be noticed that the formaldehyde has been changed into formic acid, or oxidation has taken place. The amount



of current passed through the circuit when compared to the number of mols oxidized is not as readily measured as with the former experiment, but this experiment shows that oxidation, and therefore reduction, with organic compounds as with inorganic compounds is accompanied by electrical changes.

If the amount of electricity in any oxidation-reduction reaction involving electrolytes be measured, it will be found that, for every mol of an element undergoing oxidation or reduction, 96,500 coulombs or a simple multiple of this quantity, are always involved. Similarly, if the charge, either positive or negative, carried by one mol of any ion in a solution be measured, it will also be found to be 96,500 coulombs or a simple multiple of this quantity. The quantity of electricity in all of these reactions appears to obey a law of definite and multiple proportions. Just as the atomic theory of matter is based upon these laws, so electricity may be regarded as atomic in character, and 96,500 coulombs represents one combining unit, or if the expression may be used, one combining weight of electricity. The smallest quantity of electricity associated with one atom of matter is generally known as an electron. The existence of the electron has been proven by the work of a number of physicists, especially by J. J. Thomson and R. A. Millikan.

Taking into consideration the definition of valence given before and the experiments and conclusions therefrom just described, it is now possible to give a general definition of valence which may be applied readily and used as simply as the older definition of valence. *The valence of an element may be defined as the number of negative electrons an atom of that element loses or gains to form chemical linkings.* In accordance with the modern developments of physics, the negative electron (or corpuscle) is accepted as a unit (or atom) of electricity. This view of valence states that

every chemical linking between two atoms involves the transfer of a negative electron from one atom to the other. This transfer of a negative electron requires, assuming the atom itself to be electrically neutral, that the atom which loses the electron acquires a unit positive charge, the atom which gains the electron, a unit negative charge.

The question now naturally arises: How is it possible to ascertain which atom is positive and which is negative in a compound? For substances which conduct the current in solution, the charges manifested by some of the atoms or groups of atoms will show directly the distribution of some of these electric charges. In general, the relative positions of the elements in the Periodic System, which is itself an expression of the chemical properties of the elements, serves as a guide in determining this point. In the horizontal rows, the elements of larger atomic weights are usually negative to those of smaller atomic weights; thus, $\overset{+}{\mathrm{N}}\mathrm{a}\bar{\mathrm{C}}\mathrm{l}$; $\overset{\equiv}{\overset{+}{\mathrm{N}}}\mathrm{H}_3$; $\overset{\equiv}{\overset{+}{\mathrm{C}}}\mathrm{H}_4$; $\overset{\#}{\overset{-}{\mathrm{C}}}\mathrm{Cl}_4$; etc. In the vertical series the main and subgroups must be considered separately.

The older terms, positive and negative elements, now acquire a more precise meaning. A positive element is one, whose atom, in chemical combination, has lost one or more negative electrons; a negative element, one whose atom in chemical combination has gained one or more electrons. When an atom is reduced, it gains negative or loses positive charges. Since, in any given compound, the atom which acquires the electron is the one which has the greater attraction for it under the given conditions, and since the loss or gain of an electron signifies that the element is either oxidized or reduced, the following generalization may be stated: That element in a compound is the positive element, which shows the smaller oxidizing or greater reducing potential (or has the smaller attraction or affinity for the negative electron); and conversely, that element which

has the greater oxidizing potential (or the greater affinity for the negative electron) is the negative element. This generalization substitutes the affinity of the elements for the electrons for the affinity of the elements toward each other as was done formerly. The relative oxidizing potentials signify the same relations as the chemical affinity of different atoms for each other. Just as with the other measures of the intensity factor of chemical energy, the use of the oxidizing potential must for the present be limited to qualitative relations with most organic substances.

It is possible to conceive of compounds in which the two elements which enter into chemical combination have oxidizing potentials so close to each other in value that two combinations are possible in which the positive and negative elements are interchanged in the two compounds. As an example of this type of isomerism, the two isomeric iodine chlorides may be mentioned. Since chlorine has the higher oxidizing potential, it is highly probable that in the more stable of the two isomers the iodine atom is positive, while in the less stable, the chlorine is positive. The formulas for the two compounds may be written $\overset{+}{\mathrm{I}}\overset{-}{\mathrm{Cl}}$ for the stable form, and $\overset{+}{\mathrm{Cl}}\overset{-}{\mathrm{I}}$ for the unstable form. When the oxidizing potentials of the elements differ very much in value, isomerism of this form would not be so likely. Thus with hydrogen chloride, the form $\overset{+}{\mathrm{H}}\overset{-}{\mathrm{Cl}}$ would very likely be so unstable that it would be impossible for it to exist under ordinary conditions, and it would therefore be unknown. It has often been observed that the conditions, such as the presence of other substances, influence the oxidizing potentials of the elements or, as formerly expressed, the affinity of the elements for each other. Likewise, the pressure and temperature of a mixture of methane and water may be such that the negative carbon of the methane is oxidized to the positive carbon of carbon monoxide or dioxide. It, therefore, seems possible that differences in conditions may

also give rise to electroisomers. Moreover, for many compounds of carbon in which several atoms of carbon are joined with each other, it is often very difficult to know which of the carbon atoms is positive.

It may also be repeated that the chemical resistance or the inertia of carbon compounds may also give rise to electroisomers, since one of the isomers while very unstable may still exist due to its extremely slow rate of decomposition.

The theory of electric dissociation of Arrhenius showed that the ions in solution carried definite charges. The number of these charges, taken in connection with the general views of positive and negative elements, and acidic and basic constituents of compounds, were found to be identical with the valence numbers of these atoms and groups. In this way arose the one direct experimental method of determining valence; the measurement of the electric charges on the ions. This method is of limited application, however, since many substances are not ionized in solution, and this gave rise to the view that if a substance did not ionize, its atoms were not united in the same way as the atoms of a substance which did ionize. The possible action of the solvent was not considered in this connection. Two kinds of valence were, therefore, adopted by a number of chemists, polar valence and non-polar valence. Since inorganic compounds, mainly, are ionized in solution, and organic compounds not ionized, this division was roughly applied in such a way that inorganic compounds were assumed to contain polar valences, and organic compounds, non-polar valences.

There are a number of arguments against the assumption of two kinds of combining forces in place of one kind (polar). The untenability of the dual view may be seen most readily with some of the phenomena of oxidation and reduction.

As already stated, the correct definition for oxidation and

reduction with inorganic compounds, as generally accepted, is unquestionably that involving a change in the electrical charges of the atoms; for oxidation, gain of positive charges, or loss of negative charges, for reduction, the reverse.

In the explanation of oxidation-reduction involving the transfer of electrons, it becomes evident that in speaking of oxidation-reduction it would be more correct to say that a particular element in a compound is oxidized or reduced. Thus in the case of the oxidation involved in changing ferrous chloride into ferric chloride, it is the iron which is oxidized, the chlorine is neither oxidized nor reduced. Because of the incorrent way of saying that a compound has been oxidized or reduced, the meaning of the terms oxidation and reduction has in many instances become vague. If electrons are not responsible for the union between atoms in molecules which are not electrolytes, the electrical definition of oxidation and reduction becomes inapplicable and it is necessary either to fall back upon some of the older definitions or to use an entirely new one for these cases. So far no new definition has been proposed, and the older definitions are still used in organic chemistry. Thus the addition of oxygen, or the removal of hydrogen, is taken to be the common characteristic for an oxidation. To illustrate this point: The conversion of methane into carbon dioxide and water by means of oxygen, would be considered oxidation, according to the older definitions. Methane can also be converted into carbon dioxide by treatment with chlorine, that is substitution, and subsequent hydrolysis, neither action being oxidation according to the older definition. Many other examples might be mentioned, and the general conclusion is arrived at, that it would be impossible to give any satisfactory definition of oxidation applicable to all cases. Furthermore, the oxidation of formaldehyde by permanganate as described before showed that the oxygen from the permanganate did not

add to the formaldehyde since the permanganate was not in the same beaker. There was a current of negative electricity flowing from the formaldehyde solution to the permanganate solution. A similar experiment may be carried out with ethyl alcohol in place of the formaldehyde. The formaldehyde and ethyl alcohol belong to the class of non-electrolytes, and unless the union between the atoms is considered polar in character, it would be very difficult to find a suitable definition or description for this form of oxidation.

Since the experimental evidence at hand is no more against than in favor of the view that electrons are responsible for valence in the case of non-electrolytes than in the case of electrolytes, while indirect evidence is in favor of this view, it is much simpler to adopt the view of one kind of force acting between atoms in all compounds, that is, that due to the electron associated with the atom. This at once furnishes one definition for all oxidation-reduction reactions applicable to all cases and easily understood.

A few words regarding the application of valence may be of value here. Valence is a number. Experimental facts have made the negative electron (the atom of electricity) the basis on which to build. From the chemical side, the valence of an atom shows the number of atoms (or groups of atoms) held in combination by that atom when the hydrogen atom as it exists in most of its compounds is taken as the positive unit (loss of one negative electron). These relations of positive and negative make it clear that in speaking of valence, it is not sufficient to give a number for its value, but that at the same time it must be stated whether the number is positive or negative, that is to say, whether negative electrons have been lost or gained in the combination of the atom in question. This has evidently developed as a matter of practical expediency from the experimental evidence upon which the theory of

valence is based. It would be possible to construct a theory of valence using as the basis the atoms of the elements which have gained the greatest number of negative electrons among all the elements in the formation of chemical linkings, and to consider all other combinations as positive valences. This treatment would simply amount to a shift of the standard of reference from what is now considered to be an electrically neutral atom, to an atom carrying the maximum number of negative charges (which is eight), and to consider the valence as positive when compared with this new zero standard. This method of treatment would obscure somewhat the relative positive and negative relations of the elements, which have been developed as the result of experience. At any rate, while it is important to point out that the standard or basis in use is arbitrary in the sense that it is based upon experimental facts which were obtained without reference to any theory of valence, in order to retain the connection between the theory of valence and other fields of science, the standard evolved will be adhered to strictly in the further developments.

Earlier in this chapter it was pointed out that change in free energy per unit (equivalent) weight multiplied by valence would give the change in free energy per molecule in the formation of the substance in question. In using valence in this way, the electropositive or electronegative character of the atom would not be included in determining the change in free energy of the molecule, since the positive or negative sign of this free energy change depends upon other factors and comparative units used and the method of calculating these values as developed historically. This statement is made to avoid confusion in the use of valence as a number (not positive or negative) in free energy calculations, and valence (relative positive and negative states of the atoms) in connection with the electron conception of valence.

Nitrogen in ammonia has a valence of $-3$, ($\overset{\equiv}{\underset{}{\mathrm{N}}}\overset{+}{\mathrm{H}}_3$). Nitrogen in nitrous acid has a valence of $+3$, ($\overset{+}{\mathrm{H}}\overset{=}{\mathrm{O}}\overset{\ddagger}{\underset{}{\mathrm{N}}}\overset{=}{\mathrm{O}}$). Nitrogen in ammonia therefore differs from nitrogen in nitrous acid by six units of valence. The great difference in the properties of the nitrogen in the two compounds is an expression of the difference in valence. (On the former non-polar view of valence, nitrogen was considered to have a valence of 3 in both compounds.) Nitrogen in nitric acid has a valence of $+5$. The difference between the nitrogen in the extreme states is eight units of valence. Oxidation of an atom consists in the loss of negative charges or the gain of positive charges, and therefore the change of nitrogen in ammonia to the nitrogen in nitric acid consists of an oxidation of eight units. The other atoms combined with the nitrogen in these compounds do not change their charges, or are neither oxidized nor reduced, oxygen having a valence of $-2$ and hydrogen a valence of $+1$ in all three.

The compounds of carbon show similar relationships. Carbon in methane has a valence of $-4$ ($\overset{=}{\underset{=}{\mathrm{C}}}\overset{+}{\mathrm{H}}_4$). Carbon in carbon tetrachloride has a valence of $+4$ ($\overset{\ddagger}{\underset{\ddagger}{\mathrm{C}}}\bar{\mathrm{C}}\mathrm{l}_4$). The difference in the valence of the carbon in the two compounds is eight units, or the carbon in carbon tetrachloride is in a state of oxidation eight units greater than that of the carbon in methane. In methyl chloride ($\overset{=}{\underset{=}{\mathrm{C}}}\overset{+}{\mathrm{H}}_3\bar{\mathrm{C}}\mathrm{l}$), the carbon atom has lost one negative electron and gained three, or its valence is $-3+1$, and its state of oxidation $-2$; in dichlormethane, the valence of the carbon is $-2+2$ and its state of oxidation 0; in chloroform, the valence of the carbon is $-1+3$ and its state of oxidation $+2$. This series of compounds shows the importance of stating in full the charges of the atoms which go to make up the valence, and it also illustrates the meaning of the term oxidation of an atom. The state of oxidation of an

atom conveys a definite meaning chemically only in comparison with the atom in the other states of oxidation. The change in the valence of the atom is the significant fact in speaking of oxidation, and while the state of oxidation may be shown by the number and sign of its valence, its importance is only clear and definite in comparison with other states of oxidation of the same atom.

In general terms, the extreme difference which an atom shows in its valence is eight units; for example, chlorine in hydrogen chloride (− 1) and chlorine in perchloric acid (+ 7); sulfur in hydrogen sulfide (− 2) and sulfur in sulfuric acid (+ 6); nitrogen in ammonia (− 3) and nitrogen in nitric acid (+ 5); carbon in methane (− 4) and carbon in carbon tetrachloride (+ 4). This difference refers to the same relation to which Mendeléeff referred in his Periodic System when he stated that the sum of the valences toward oxygen and toward hydrogen of the elements of the V, VI, and VII Groups was equal to eight. The compounds of the elements of the I, II, and III Groups in which they gain negative electrons are at present not sufficiently well defined and extensively studied to indicate the general relations existing there.

As a matter of convenience, the direction in which the negative electron is transferred in the formation of a chemical linking may be indicated by an arrow, as suggested by J. J. Thomson, the head of the arrow giving the direction of the transfer of the electron. The lines representing linkings as written heretofore in structural formulas will therefore be replaced by arrows; H → Cl in place of H − Cl, etc. This saves the cumbersome use of plus and minus signs, but in case of doubt or for the sake of clearness, it is also advisable to use these signs in connection with the formulas.

## CHAPTER II.

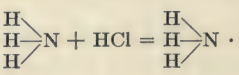
### VALENCE (CONTINUED); CO-ORDINATION NUMBER.

It has been emphasized that in simple compounds the valence is the capacity of an atom of one element to hold in chemical combination a certain number of atoms of some other element. It will now be necessary to consider another form of combining capacity which appears to manifest itself in the case of molecules of compounds combining with definite numbers of molecules of some other compound. As examples may be mentioned hydrates such as $CaCl_2.6H_2O$, $CrCl_3.6H_2O$, $CuSO_4.5H_2O$; ammoniates such as $AgCl.2NH_3$, $CuSO_4.4NH_3.H_2O$; and double salts such as $4KCN.Fe(CN)_2$, $2KCl.PtCl_4$. These compounds have as components simpler compounds which are combined in definite proportions just as the elements in the simpler compounds are combined in definite proportions. It becomes evident, therefore, that apparently combining capacities of molecules for other molecules exist here in much the same way as in the case of the combining capacity of atoms for other atoms.

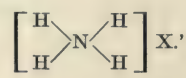
A. Werner, in the last twenty years, has systematized compounds of varying degrees of complexity. In order to explain the formation of addition compounds, as for example, sulfur trioxide with water, ammonia, hydrogen chloride, etc., platinic chloride with ammonia, water, hydrogen chloride, etc., ammonia with water, hydrogen chloride, etc., he makes the assumption that various atoms such as the sulfur in the sulfur trioxide, the platinum in the platinic chloride, and the nitrogen in the ammonia, etc., possess a residue of unsaturated affinity, which permits such groups to mutually satisfy each other. When the amount of this affinity is sufficient to bring about a stable

combination between the single molecules, it assumes practically the same rôle as the ordinary valence, viz; it effects an interdependence between two elementary atoms, and in this way unites two radicals to a molecular complex. These new valences differ, however, from ordinary valences, in that they are not able to unite univalent radicals and in order to distinguish them from the latter he calls them "auxiliary valences."

In the case of ammonium chloride, the unsaturated auxiliary valence of the nitrogen atom in the ammonia would be saturated by the auxiliary valence of the hydrogen atom of the hydrogen chloride. The formation of the ammonium chloride would be formulated therefore as



"Since according to this formula, four hydrogen atoms are bound to nitrogen, it is hardly to be supposed that one hydrogen atom is linked up by a greater amount of affinity than any of the remaining three; it is far more probable that a state of equilibrium is reached in which all the hydrogen atoms are linked by the same amount of affinity. Ammonium is therefore a complex radical, $NH_4$, in which the nitrogen is the central atom having the four hydrogen atoms linked to itself with the same amount of affinity in each case. On each hydrogen atom of the complex $NH_4$, there is still a certain amount of unsaturated affinity, which the radical is able to utilize externally to itself and becomes in this way monovalent. Ammonium salts have, therefore, the following structure:

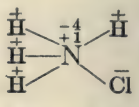
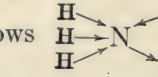


E. C. C. Baly approached this general question in a different way. His views may be stated briefly as follows

(Jour. Amer. Chem. Soc. *37*, 979 (1915)): From the study of the absorption in the ultraviolet region of the spectrum of reacting substances before, during, and after the reaction, he concluded that every chemical molecule is surrounded by a condensed force field of electromagnetic type. If molecules of different substances are brought close together, they tend to form an associated system, or addition compound, with a loss of energy, and establishment of potential gradient. If this potential gradient is steep enough, a transfer of electrons will occur with the formation of a true chemical compound. Thus the compounds HX and YOH may unite to form HX.YOH, and then rearrange to $XY.H_2O$, a system containing less energy than HX.YOH. If the force lines of the two molecules form completely closed systems, no reaction will occur between them until their force fields are opened up, perhaps by molecules of some other substance as the solvent or a catalyst.

It is apparent that a similarity exists between the views of Werner and of Baly concerning the mechanism involved in the formation of these addition compounds. Both consider that simple compounds such as ammonia and hydrogen chloride possess unsaturated properties, Werner, auxiliary valence, and Baly, open force fields, which enable these compounds to combine to form addition compounds. According to Werner, after the two simple compounds come together, there is a readjustment of this affinity, or auxiliary valence, between the nitrogen atom of the ammonia and the hydrogen atom of the hydrogen chloride in such a way that all the hydrogen atoms in the ammonium chloride are united to the central nitrogen atom in the same way, while the chlorine atom is held finally by the new residual affinities of the four hydrogen atoms in the $NH_4$ radical. Baly considers that after the force fields have brought the two simple compounds together in the case of a compound like ammonium chloride, there is a

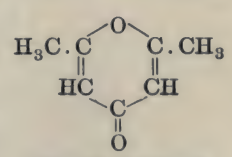
readjustment of these forces, causing a formation of the stable compound.

If the valences in the ammonium chloride are assumed to be due to electrons as described in the first chapter, then the structure of the compound would be  or, indicating the direction of transfer of the negative electrons by means of arrows  . This formula for the structure of ammonium chloride has all the advantages of the Werner formula, viz; it agrees with the results of V. Meyer and M. Lecco's (Lieb. Ann. *180*, 173 (1876)) experiments that the four hydrogens bear the same relation to the molecule, and it shows that the chlorine bears a different relation to the nitrogen than the hydrogen. Furthermore, it has the advantage over Werner's formula in that only one kind of valence is necessary. Also, it is readily seen that neither oxidation nor reduction is involved in the formation of an addition compound of this type. If only the auxiliary valence idea of Werner is used in this connection, the positions of the electrons are not definite, so that it would be difficult to state by means of the structures whether any oxidation or reduction had occurred.

Many compounds similar to ammonium chloride, such as derivatives of the amines, have been prepared and studied. These compounds were for some time thought to follow the law of definite proportions. For example, an equal number of molecules of amine and acid combined to form the definite substituted ammonium salts. Although this generalization appeared to hold for a number of such compounds, other substances were prepared after a time in which these simple relations were not observed. Thus, the compound $(NH_3)_4HCl$ (cf. Werner, Neuere Anschauun-

gen) was prepared, then compounds such as $AgCl(NH_3)_2$, $PtCl_4(NH_3)_2$, $PtCl_4(NH_3)_6$, $CuSO_4 4NH_3 H_2O$, etc., which did not follow such simple laws, and for which the ordinary ideas of valence did not suffice. Some of these compounds were in fact termed "anomalous," because they did not fall into a scheme of simple formulas as it was expected they should. It was thought that the reaction between ammonia or an amine, and hydrochloric acid, was similar to the reaction between a base and an acid to form a salt, but the combinations between ammonia and salts to form the compounds just indicated showed that this was not the case and that ammoniates, as these compounds are called, did not require the participation of an acid.

C. Friedel, in 1875 (Bull. Soc. Chim. [2] *24*, 160, 241), showed that in cooling a solution of hydrogen chloride in ether, a crystalline compound was formed containing an equal number of molecules of ether and of hydrogen chloride. This observation was an isolated one for some years. J. N. Collie and T. Tickle (Trans. Chem. Soc. *75*, 710 (1899)) found that dimethyl pyrone formed compounds with the halogen hydrides which showed the properties characteristic of ammonium halides, and later were found to ionize in solution in a manner similar to ammonium salts, and were therefore comparable to them. A. Baeyer and V. Villiger (Ber. *34*, 2679 (1901)) then made an extended study of the salts formed with a number of acids by different groups of oxygen compounds including ethers, ketones, esters, etc. These salts or oxygen compounds are analogous to the nitrogen (ammonium) compounds. They are not as stable under ordinary conditions, and their isolation and preparation in quantity for study is difficult for most of them. Certain acids have been found to be especially suitable for the preparation of these stable oxonium salts,



Dimethyl pyrone

hydroferrocyanic acid (by Baeyer and Villiger) and perchloric acid (by K. A. Hofmann, Ber. *43*, 1080 (1910)). In order to determine whether definite compounds are formed, it is necessary to study the "Property-Composition Curves" of mixtures of their components, such as, for example, the freezing-point curves.

The application of the principles of the Phase Rule (cf. A. Findlay's "Phase Rule," or any of the larger modern text-books of general chemistry) shows the existence of such oxonium salts and their composition, since it may be stated in general terms, that each maximum point of such a freezing point curve plotted with abscissas as relative content of the two components in the mixture and ordinates as the freezing points, shows such a compound of the composition given by the point on the abscissa axis. The application of such studies (and of analogous studies on the properties depending upon thermodynamic relations such as vapor pressure, etc.) to aqueous solutions indicated that compounds of water and salts exist similar to the ammoniates. It is readily conceivable that the hydrate of hydrogen chloride may be compared with ammonium chloride, some of the chemical properties differing because of the difference between nitrogen and oxygen. This question will be taken up again later. For the present, reference to a number of papers describing such compounds may be given.

Among those who have worked in this field may be mentioned J. N. Collie and T. Tickle, Trans. Chem. Soc. *75*, 710 (1899); J. N. Collie, Ibid. *85*, 971 (1904); A. Baeyer and V. Villiger, Ber. *34*, 2679, 3612 (1901); *35*, 1201 (1902); S. Hoogewerff and W. A. van Dorp, Rec. trav. chim. *21*, 349 (1902); J. Thiele and F. Strauss, Ber. *36*, 2375 (1903); D. Vorländer, Lieb. Ann. *341*, 1 (1905); V. A. Plotnikoff, J. Russ. phys. chem. Ges. *36*, 1088 (1904); *40*, 64 (1908); H. Stobbe, Lieb. Ann. *370*, 93 (1909); K. A. Hofmann and co-workers, Ber. *43*, 178, 183, 2624 (1910); D. McIntosh,

Jour. Amer. Chem. Soc. *32*, 542 (1910); O. Maass and D. McIntosh, Ibid. *34*, 1273 (1912); *35*, 535 (1913); M. Gomberg and L. H. Cone, Lieb. Ann. *376*, 183 (1910); J. Kenda'l, Jour. Amer. Chem. Soc. *36*, 1222, 1722 (1914); J. Kendall and C. D. Carpenter, Ibid. *36*, 2498 (1914); J. Kendall and W. A. Gibbons, Ibid. *37*, 149 (1915); as well as a number of others.

Water, then, may add to salts to form the so-called "water of crystallization" or hydrates in a way similar to the action of ammonia.

The structures of some of the simpler molecular compounds will now be developed before going on to the more complex ones and the double salts. Ammonia is formulated $\overset{\equiv}{\underset{\equiv}{N}}\overset{+}{H}_3$, hydrogen chloride, $\overset{+}{H}\overset{-}{Cl}$, and ammonium chloride, $\overset{\equiv}{\underset{\equiv}{N}}\overset{+}{H}_4\overset{-}{Cl}$. The state of oxidation of nitrogen in ammonia and in ammonium chloride is the same, $-3$ and $-4+1=-3$. The difference in the nitrogens consists in the fact that one negative electron was taken up and one given off in the formation of the ammonium salt. A comparison of the similar simple molecular compounds of other elements brings to light the same fact, that in each the "central" element takes up and gives off a negative electron in forming the molecular compound but does not change its state of oxidation. Thus, there may be mentioned phosphonium (state of oxidation of phosphorus $-4+1=-3$), sulfonium $(-3+1=-2)$, oxonium $(-3+1=-2)$, iodonium $(-2+1=-1)$, selenonium $(-3+1=-2)$, arsonium $(-5+1=-4)$, stannonium $(-3+1=-2)$, and stibonium $(-5+1=-4)$ compounds.

The characteristic property of these simple molecular compounds, which may be grouped under the name of "onium compounds," is the fact that the atoms or groups combined directly with the "onium" forming or central element, act as a unit with the central atom in many physical and chemical transformations and are often termed

radicals. This is shown for physical phenomena in the conduction of the electric current where these groups act very often as ions, and in chemical reactions in metatheses where the groups are capable of replacing other atoms or groups.

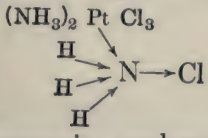
When ammonia is added to platinic chloride, it appears that two methods of combination exist. The first two molecules of ammonia add to form the compound $PtCl_4.2NH_3$, which is not ionized in solution, and does not yield a precipitate of silver chloride when treated with silver nitrate. If a compound containing a third molecule of ammonia is prepared, $PtCl_4.3NH_3$, this substance ionizes and one of the four chlorine atoms may be precipitated by silver nitrate. The third ammonia molecule evidently exerts a different influence in the molecule than the other two. In the substance $PtCl_4.4NH_3$, two chlorine atoms are ionized, while in $PtCl_4.6NH_3$, four chlorines are ionized. The last four ammonia molecules play a different part from the first two in causing the chlorine to assume new properties. The hydrates of chromic chloride show similar phenomena. The electrical conductivity of the greyish blue hydrate, $CrCl_3.6H_2O$, is practically constant, four ions are present, and all the chlorine may be precipitated with silver nitrate. In a freshly prepared solution of the isomeric green compound at 0°, only one third of the chlorine is precipitated by silver nitrate, and the conductivity at first is much less than that of the former, but increases gradually, until it finally reaches the same value as that of the other isomer. The chlorine in these two compounds is evidently combined differently. Three hydrates of chromic chloride, having the composition $CrCl_3.6H_2O$, are known. In one, one chlorine may ionize, in another two chlorines ionize, and in the third all the chlorines are ionic in solution (cf. Werner, Neuere Anschauungen, III Edition, (1913) p. 333).

It has been stated that platinic chloride will add ammonia just as hydrogen chloride does. The only difference at the

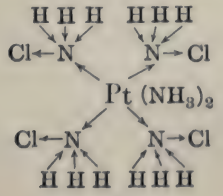
present time is that the ammonia can exert two distinct influences or can add in two ways in connection with platinum chloride, while it is probable that it can add in one way only to hydrogen chloride, although an allotropic modification of ammonium chloride was described recently (F. E. C. Scheffer, Chemical Abstracts *10*, 411 (1916)).

Ammonium chloride in aqueous solution yields chlorine ions just as the platinum chloride-ammonia compound, $2NH_3.PtCl_4$ with 1, 2, 3, or 4 additional molecules of ammonia does. Since ionization was pointed out as a characteristic property determining in which way the ammonia had added to the platinic chloride or the influence it exerted in the compound, it is likely that the ammonia in the ammonium chloride is combined with the hydrogen chloride in the same way that the ammonia is combined with the platinic chloride when the chlorines of the latter become ionic. If, therefore, the structure of ammonium chloride is known, it is possible to assign a structure to the addition compounds of platinic chloride and ammonia as far as the ammonia molecules which cause the chlorine atoms to become ionic are concerned.

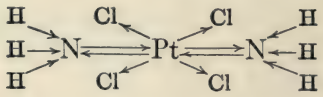
Since diammono platinic chloride, $(NH_3)_2PtCl_4$, combines with ammonia in a similar way to that of hydrogen chloride, the structure of the addition product may be written in a similar way, namely




Introducing successive molecules of ammonia, analogous structures follow, until when all four chlorines are ionizable, the structure

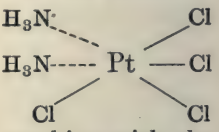


or $(NH_3)_2Pt(\rightarrow \overset{\equiv}{\underset{+}{N}}H_3 \rightarrow \bar{C}l)_4$ is obtained. The question which now presents itself is the way in which the other two molecules of ammonia are combined in the last compound and also in $(NH_3)_2PtCl_4$. The only evidence which is available is that starting with platinic chloride, in which the valence of the platinum is + 4, no oxidation or reduction of any of the atoms is observable when the successive molecules of ammonia are added. Platinic chloride is also capable of adding two molecules of hydrogen chloride, forming $H_2PtCl_6$, in which two hydrogen atoms are ionizable. This last reaction indicates that platinum, like nitrogen, is capable of acting as an onium element, forming molecular compounds. If this assumption is made, then the structures of the combinations can be expressed as




etc. In this way, only one kind of valence is present, and, so long as no evidence exists against these structures, and evidence (partly indirect, it is true) in favor of them, they will be adopted.

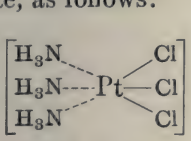
In writing the structures of addition compounds, Werner indicates auxiliary valence by dotted lines and ordinary valence by full lines. This is illustrated by his structure

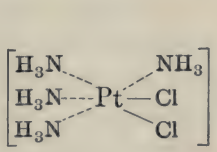


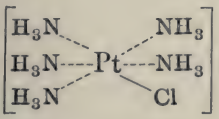

for the di-ammoniate of platinic chloride, $H_3N$----- Pt —Cl

When additional molecules of ammonia combine with the di-ammoniate, Werner considers these ammonia molecules to be held by auxiliary valences in the same way as the first two ammonia molecules, or in other words, that ammonia adds to the platinum in one way only. This is different from the idea developed here. Since the addition

of the third, etc., molecules of ammonia give rise to ionic chlorine, Werner considers that the entering ammonia takes a position between the platinum atom and the chlorine atom, crowding the latter away from the central platinum atom into a separate zone. Since the distance of the chlorine atom from the central platinum is greater than when it is bound directly, the latter acquires different chemical properties, which manifest themselves in the ionic character of the chlorine, etc. (Werner). Thus, the indirect union is characterized by ionic properties. Atoms which are directly attached to another atom either by principal or auxiliary valence are in the first zone. The number of atoms or of molecules in the first or inner zone determines the "Co-ordination Number." Atoms which are indirectly joined to the central atom are in the second or outer zone. Werner writes the structures for the ammoniates of platinic chloride containing more ammonia than di-ammoniate, as follows:



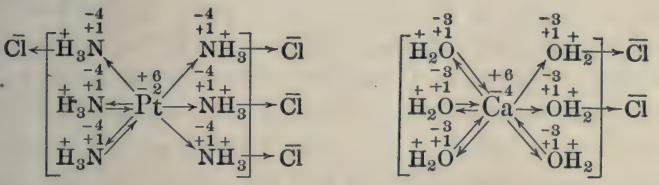




The question of nomenclature is an important one and must be considered in this connection. Werner introduced certain terms in the development of his theory involving main and auxiliary (or secondary) valences, and these terms are useful. The consideration of a group in a molecule in which the atoms react as a unit, as the inner zone or sphere, and another group as the outer zone is used by Werner, the former to denote the group consisting of the central atom combined with other atoms or groups by

auxiliary or principal valences and ionizing in solution. The method introduced by Werner of writing these groups is extremely convenient, the inner zone being enclosed in brackets. The expressions inner zone and outer zone and the use of brackets will be followed in this book, but the significance of the combinations between the atoms from the point of view of the electron conception of valence must be kept strictly in mind. In using the terms introduced by Werner, it is not intended to endow the groups with the physical significance which the meanings of the words might imply. The expressions inner zone and outer zone simply mean different groups which have a partially independent existence under special conditions (the most common one being in solution), and the atoms comprising such a group act as a unit very often. The terms inner and outer mean nothing more and must be looked upon as a convenient phraseology.

The force field theory of Baly assumes the primary formation of an addition product, which, under certain conditions can become a definite compound in which the atoms are combined by ordinary valences. The views outlined here may be used similarly. The first addition of ammonia and hydrogen chloride may produce a compound $H_3N \rightleftarrows HCl$, or $H_3N \rightleftarrows ClH$, presumably the former by analogy as will be pointed out later, and this then rearranges or tautomerizes to the more usual form $H_4NCl$. These two steps correspond to the steps of Baly. The onium valence corresponds in a number of compounds to the auxiliary valence of Werner, and the reaction just given may be stated in Werner's terms as due to a compound being formed of molecules combined by an auxiliary valence, which under certain conditions may become principal valences. The views given here have an advantage over other views in postulating only one kind of valence, and in keeping the difference between valence and chemical affinity strictly in mind.

The structures developed with platinic chloride can evidently be applied to a great number of compounds, such as hydrates, other ammoniates, and molecular compounds in general. A comparison of the structures of hexammono-platinic chloride and the hexahydrate of calcium chloride will show this:



From the foregoing it is evident that the co-ordination number of the platinum in platinic chloride di-ammoniate, $(NH_3)_2PtCl_4$, or in platinic chloride hexa-ammoniate, $(NH_3)_2PtCl_4 4NH_3$, is six, while the co-ordination number of nitrogen in ammonium chloride is four, etc.

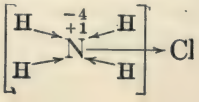
Calcium chloride may combine with six, four, or two, molecules of water of hydration or exist in the anhydrous state. The co-ordination number of the calcium in the hexahydrate is six, but what it is in the tetrahydrate is difficult to say, since it is not known whether the chlorine is in the inner or outer zone. In the di-hydrate it may be four, and in the zero hydrate it can only be two. The external physical conditions such as concentration, vapor pressure, and temperature, determine the number of molecules of water of hydration of the calcium chloride. This shows that the co-ordination number of the calcium is dependent upon external conditions just as the ordinary valence is.

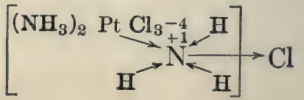
Calcium chloride combines with eight molecules of ammonia, or the calcium has the co-ordination number eight in this compound. A large number of salts have been found to crystallize with six molecules of water. With regard to ammonia, copper sulfate can combine with four

molecules, silver chloride with two, etc. Werner showed that the co-ordination number of an element is, in general, four, six, or eight.

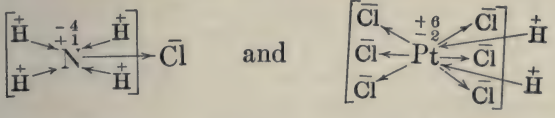
These definite numbers show a capacity for combination and are therefore of the nature of valence numbers. They are not identical with the atomic valence as already defined, which is due to the transfer of a negative electron, but indicate a different kind of capacity factor of chemical energy. The manner in which this is to be interpreted, and the underlying properties upon which it depends, cannot be settled at present. A possible suggestion that it depends upon spacial configuration and arrangement of the atoms around a central atom may be put forward. The stereochemistry of the compounds, as shown by A. Werner, the deductions of T. V. Barker, and the theoretical and experimental researches of W. H. and W. L. Bragg and of A.C. Crehore, point in this direction. Whatever the cause may be, this capacity factor exists, and as shown, may be interpreted by means of the general valence linkings of the electron conception. In the later chapters, the significance of co-ordination number in this sense is used where reference is made to a definite combining capacity of this nature.

Although the platinum atom in the ammoniates of platinic chloride has been considered as the central atom, the nitrogen of the ammonia (except with the first two molecules of ammonia) also may be taken to be the central atom. Thus, when the di-ammoniate, $(NH_3)_2PtCl_4$, combines with ammonia, it really plays the same part as the hydrogen chloride in the formation of ammonium chloride. In both cases, the chlorine of the hydrogen chloride and of the di-ammoniate, $(NH_3)_2PtCl_4$, becomes ionic. The structures for the tri-ammoniate, $(NH_3)_2PtCl_4NH_3$, and ammonium chloride are analogous:



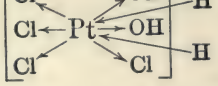
When hydrogen chloride and platinic chloride combine to form the addition compound, chlorplatinic acid, $H_2PtCl_6$, the platinic chloride plays a rôle somewhat similar to that of ammonia in the formation of ammonium chloride, that is, both are added to hydrogen chloride. There is a difference, however, in that the addition of platinic chloride to hydrogen chloride causes the hydrogen of the hydrogen chloride to become ionic, while the addition of ammonia to hydrogen chloride causes the chlorine of the hydrogen chloride to become ionic. In other words, in the first case, the hydrogen is in the outer zone; in the second, the chlorine is in the outer zone. Since ionogens are produced in both cases, both the ammonia and the platinic chloride, according to Werner, enter between the hydrogen and the chlorine atoms in the hydrogen chloride. In one case, the hydrogen is crowded out into the outer zone, while in the other, it is the chlorine of the hydrogen chloride. Accordingly, the structures of the two compounds may be written



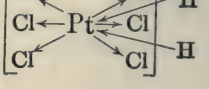
The two complexes, ($PtCl_6$) and ($NH_4$), bear the same relation in the addition compounds, the only difference being that the charges have different signs, the former being negative and the latter positive. The reason for this lies in the electrical nature of the two central atoms. Platinum is an electro-positive element, and nitrogen in ammonia is an electro-negative element. It becomes evident in looking over a large number of complex salts, that they ionize in such a way that the element in the outer zone has an electric charge of the same sign as that of the central atom to which it is attached. Thus, in addition, of those with positive central atoms, potassium ferro- and ferri-cyanides, where the positive iron atom serves as the

central atom, potassium chromium oxalate, $K_3Cr(C_2O_4)_3$, may be quoted out of the great number with which the reader, no doubt, is familiar. As compounds of the type in which the central atom is negative, may be mentioned besides ammonium chloride, and the tri-ammoniate, tetra-ammoniate, etc., of platinic chloride, the hydrates of calcium chloride, aluminium chloride, chromium chloride, etc., since in these hydrates just as in the ammoniates, the oxygen of the water may serve as the central atom.

It has been stated that water like ammonia can be added in two ways in the formation of addition compounds such as the hydrates, calcium chloride hexahydrate, etc., similar to the ammonia in the hexa-ammoniate of platinic chloride, $PtCl_46NH_3$. When platinic chloride is dissolved in water, the aqueous solution does not contain chloride ion as would be expected if the water combined with the chloride as the ammonia does. The platinic chloride combines with the water, however, to form the di-hydrate, $PtCl_42H_2O$, which is an acid and yields the ions $2\overset{+}{H}$ and $PtCl_4(OH)_2^{=}$, and should therefore be formulated $H_2PtCl_4(OH)_2$. The water behaves towards the platinic chloride just as the hydrogen chloride does in the formation of the chlorplatinic acid, $H_2PtCl_6$. The platinic chloride enters between the hydrogen and the hydroxyl of the water molecule, analogous to the way it does in the case of hydrogen chloride, and in each case forces or transfers the hydrogen into the outer zone. The structures of the two complexes, $PtCl_4(OH)_2$ and $PtCl_6$, ought therefore to be alike. They may be written as follows:



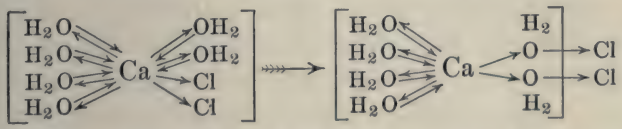

and



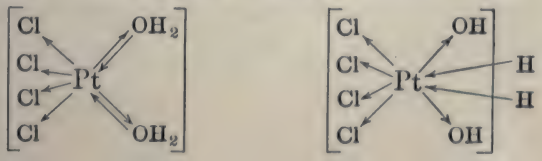

I II

The water molecule here has added as H and OH. In order

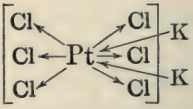
to get a definite picture of the differences between the three ways in which water can function in these addition compounds, the reader may compare structure I with the structure of the hexa-hydrate of calcium chloride. With the latter, part of the water enters between the calcium and chlorine atoms, producing chloride ions, and part of the water is simply added to the calcium atom by onium valence or "auxiliary" valence or "force field," symbolized by the two arrows in opposite directions. It was stated previously that the first stage in the formation of ammonium chloride from ammonia and hydrogen chloride may be the formation of a primary addition compound, $H_3N \rightleftarrows HCl$, due simply to the onium valence, or the auxiliary valence or the force field between the nitrogen and the hydrogen atoms, and that this preliminary compound then tautomerizes into $(NH_4)Cl$ with the chlorine in the outer zone. Now this preliminary stage possibly may occur in the formation of all these addition compounds, no matter what the subsequent rearrangement happens to be. Thus, in the formation of the hexa-hydrate of calcium chloride, all the molecules of water first may add to the calcium atom through the force field, and then tautomerism may set in, the chlorine leaving the calcium to combine with the oxygen of the water.




Similarly with the di-hydrate of platinic chloride, $H_2PtCl_4(OH)_2$, all the water molecules may add to the platinum atom through the force field first and then rearrangement set in and the hydrogens become ionic.

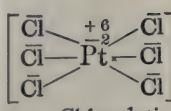


In the case of the hexa-ammoniate of platinic chloride, the ammonia may behave in a way analogous to that of the water in the hexahydrate of calcium chloride. Whether or not all the water molecules or ammonia molecules must first be combined with the platinum or calcium atoms in this way before any tautomerism can take place, it is impossible to say.

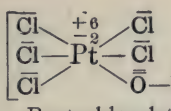
Potassium chloride adds to platinic chloride, in the same way that hydrogen chloride does, forming potassium chlorplatinate. The latter would therefore have a structure similar to that of the acid, or:  Just as in the case of the formation of the other addition compounds, here, too, probably, the intermediate stage may occur where the potassium chloride is added to the platinum atom in the onium way and then rearranges, the potassium going into the outer zone.

It is well known that ammonium chloride can add to platinic chloride just as potassium chloride does, forming the ammonium chlorplatinate. Chlorplatinic acid, $H_2PtCl_6$, adds to ammonia just as hydrogen chloride does, forming the ammonium chlorplatinate; the di-ammoniate of platinic chloride adds to hydrogen chloride, forming ammonium chlorplatinate. In each of the above cases an addition compound plays the same rôle as a simple compound, forming addition compounds with other molecules.

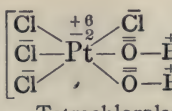
From what has been said in regard to the probable structures of the hexachlorplatinic acid, $H_2PtCl_6$, and the tetrachlorplatinic acid, $H_2PtCl_4(OH)_2$, it is possible to assign structures to the whole series of platinic acids, as Werner has done (Neuere Anschauungen auf dem Gebeite der anorganischen Chemie, 3d ed. (1913), pp. 40–1).



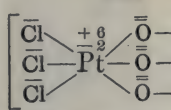
Chlorplatinic acid



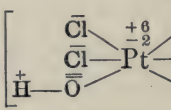
Pentachlorplatinic acid



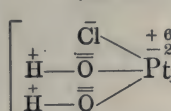
Tetrachlorplatinic acid



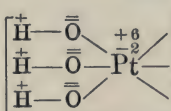
Trichlorplatinic acid (not known)



Dichlorplatinic acid



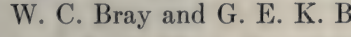
Monochlorplatinic acid



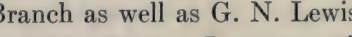
Platinic acid

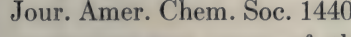
The fact that these acids are all dibasic proves that the acidity is not connected with the hydrogen of the hydroxyl groups, and by comparing the whole series from chlorplatinic acid to platinic acid, it is evident that the ionizable hydrogens are those combined directly with the positive central atom, platinum in this case. The salts of these acids have similar structures.

It will have been observed that tautomerism has been spoken of a number of times as occurring with different compounds. The idea of tautomerism is familiar from organic chemistry, but it appears to be of much wider applicability than has been heretofore assumed (cf. also W. C. Bray and G. E. K. Branch as well as G. N. Lewis, Jour. Amer. Chem. Soc. 1440–1455 (1914)). In tautomeric rearrangements, none of the atoms in the molecules is reduced or oxidized; each remains in the same state of oxidation as before. This is brought out by the following formulas which represent the tautomeric forms of a number of substances:



and





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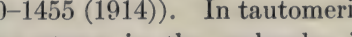


$\overset{+}{H}_3\overset{-4}{\underset{+1}{N}} \rightleftarrows \overset{+7}{\underset{-1}{S}}\overset{-2}{O}_3$ and $\overset{+}{H}_2\overset{-3}{N} \leftarrow \overset{+6}{S}\overset{-2}{O}_2 \rightarrow \overset{-2}{O}\overset{+}{H}$

$(\overset{+}{H}_3\overset{-4}{\underset{+1}{N}})_3 \rightleftarrows \overset{+7}{\underset{-3}{Pt}}\bar{C}l_4$ and $(\overset{+}{H}_3\overset{-4}{\underset{+1}{N}})_2 \rightleftarrows \overset{+6}{\underset{-2}{Pt}}(\bar{C}l_3) \rightarrow \overset{-4}{\underset{+1}{N}}\overset{+}{H}_3 \rightarrow \bar{C}l$

$(\overset{+}{H}_2\overset{-3}{\underset{+1}{O}})_2 \rightleftarrows \overset{+6}{\underset{-2}{Pt}}\bar{C}l_4$ and $\overset{+}{H}_2\overset{+6}{\underset{-2}{Pt}}\bar{C}l_4(\overset{-2}{O}\overset{+}{H})_2$,

and so on.

These examples show the possibilities of tautomerism in inorganic compounds. The valence or state of oxidation of none of the atoms has changed. Although tautomeric changes in molecules will be used in the later chapters, it will not be referred to explicitly or in detail.

## CHAPTER III.

### ACIDS AND BASES.

The valence views upon which the structures and classification of substances depend have been given in some detail in the preceding chapters. Before proceeding to consider the theory of chemical reactions which it is desired to emphasize here, some further applications of the valence views may be of interest. Acids and bases form two of the most interesting and widely studied groups of substances in chemistry, and the bearing of the theoretical relations described upon their reactions and formulations will be given. The considerations bear also upon the state of substances in solution.

The theoretical view of the chemical nature of acids was put upon a very much more satisfactory scientific basis by Arrhenius in 1887. He showed that the acid properties of substances in solution depended upon the presence of hydrogen ion, and that the concentration of this hydrogen ion could be measured in a number of different ways. In the electrolytic dissociation in solution in which the positive hydrogen ion is produced, the rest of the molecule forms the negative ion, but for the characteristic properties of the acid only the hydrogen is of importance.

The theory of ionization in solution showed that hydrogen ions are the essential constituents of acids. However, the part played by the solvent in the ionization, or in other words, the probable mechanism of reaction according to which the ions are produced, is not shown in the theory of Arrhenius. It is true that the relative degrees of ionization of substances in different solvents were shown to be paralleled by certain other properties of the solvent, such as the dielectric constant, and that combination of the solvent

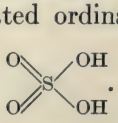
with the ion has been proven to exist in a number of cases, but these facts are far from a satisfactory theory of the reactions taking place when a substance is considered to undergo ionization.

The views of Werner with regard to acids may be stated in the form in which he summarized them (Neuere Anschauungen, pp. 273–275), (1) There are anhydro acids and aquo acids. (2) Every compound which can form a hydrate with water, and which then yields hydrogen ions in aqueous solution as a product of ionization, is an anhydro acid. (3) Every hydrate which ionizes in aqueous solution yielding hydrogen ions, is an aquo acid, or in short, an acid. In terms of the ionic electrochemical viewpoint, the following definition is given by Werner for an anhydro acid: A compound which, in aqueous solution, combines with the hydroxyl ions of the water, and in this way shifts the equilibrium for the electrolytic dissociation of water to a limiting value for the hydrogen ion concentration characteristic for the compound, is an anhydro acid.

These views of Werner, involve a theory of the mechanism of acid production in solution, and are of general interest. The structures which he gives are of the same nature as those he gives for salts, etc., as will be seen presently when comparing them with the structures developed in connection with the electron conception of valence.

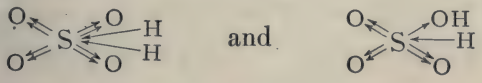
The views with regard to acids which follow from the electron conception of valence and from the principles outlined in the earlier chapters will now be given.

It will be of interest to take up a number of acids containing oxygen. Sulfuric acid may serve as a typical example. Its structure is formulated ordinarily as:




This structure is based upon a number of experimental

facts, such as the reactions of organic derivatives of the acid and related compounds, the successive replacement of the hydroxyl groups, etc. From the discussion of the platinum acids in the preceding chapter, it appears to be highly improbable or a substance possessing this structure to ionize as an acid. If, however, the structure is written in the tautomeric form, this difficulty disappears and sulfuric acid falls in line with the platinum acids. The tautomeric forms of sulfuric acid are:



The formation of dibasic acids through the addition of water to both sulfur trioxide and platinic chloride becomes, from the above considerations, a similar phenomenon. According to the older view, the formation of sulfuric acid from sulfur trioxide and water is due to the opening up of one of the double bonds between the sulfur and one of the oxygen atoms, and the addition of the water as hydrogen and hydroxyl to this opened up group.

$$O_2S{=}O \rightarrow O_2S{-}\underset{|}{O}{+}H{-}OH \rightarrow O_2S\begin{matrix}OH\\OH\end{matrix}$$

This explanation cannot be applied to the mechanism involved in the formation of the tetrachlorplatinic acid, $H_2PtCl_4(OH)_2$.

The addition of hydrogen chloride to sulfur trioxide, becomes analogous to the addition of hydrogen chloride to platinic chloride, yielding in the first case, chlorsulfonic acid, $HSO_3Cl$, and in the second case, chlorplatinic acid, $H_2PtCl_6$.

The addition of potassium chloride to platinic chloride to form potassium chlorplatinate, $K_2PtCl_6$, is similar to the formation of potassium sulfate from potassium oxide and sulfur trioxide.

The addition of ammonium chloride to platinic chloride to form ammonium chlorplatinate, $(NH_4)_2PtCl_6$, is similar to the reaction between chromium trioxide and ammonium chloride to form $CrO_3ClNH_4$ (Werner). (It is impossible to go into all the examples which may be given along these lines, and the reader is referred to Werner's book for more complete information.)

It is possible to formulate the reaction involved in the formation of the first stage addition compound, in the case of many of these substances as follows:

$$SO_3 + H_2O \rightleftharpoons SO_3 \rightleftarrows H_2O, \qquad SO_3 + HCl \rightleftharpoons SO_3 \rightleftarrows HCl,$$

$$SO_3 + NH_3 \rightleftharpoons SO_3 \rightleftarrows NH_3,$$

$$PtCl_4 + 2H_2O \rightleftharpoons PtCl_4 \begin{matrix} \rightleftarrows H_2O \\ \rightleftarrows H_2O \end{matrix},$$

$$PtCl_4 + 2HCl \rightleftharpoons PtCl_4 \begin{matrix} \rightleftarrows HCl \\ \rightleftarrows HCl \end{matrix},$$

$$PtCl_4 + 2NH_3 \rightleftharpoons PtCl_4 \begin{matrix} \rightleftarrows NH_3 \\ \rightleftarrows NH_3 \end{matrix},$$

$$PtCl_4 + 2KCl \rightleftharpoons PtCl_4 \begin{matrix} \rightleftarrows KCl \\ \rightleftarrows KCl \end{matrix},$$

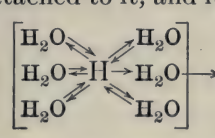
$$AuCl_3 + KCl \rightleftharpoons AuCl_3 \rightleftarrows KCl,$$

$$AuCl_3 + NH_4Cl \rightleftharpoons AuCl_3 \rightleftarrows NH_4Cl,$$

etc.

These primary addition products may then rearrange or tautomerize into the structures for the acids or salts which have already been given and which represent the customary formulations.

It has been mentioned that addition compounds which consist of more than one zone are ionogens by definition or description, and that if the components in one zone are hydrogen or hydrated hydrogen, the compound is an acid. The hydrogen bearing this relation to the addition com-

pound corresponds to the hydrogen ion of Arrhenius. A substance dissolved in water will be an acid (that is, it will furnish hydrogen ion $H^+$) if it forms hydrates containing hydrogen or hydrated hydrogen in one of the zones. For example, hydrogen chloride forms hydrates when dissolved in water and is an acid, but when dissolved in some solvent with which it does not form an addition compound, a hydrocarbon for example, then it does not have the properties of an acid. The hydrate of hydrogen chloride in dilute aqueous solution will undoubtedly have a great number of water molecules attached to it, and its probable structure may be expressed as  The part within the brackets is, therefore, an example of hydrated hydrogen.

Hydrogen chloride may also form an acid by combining with other compounds than water. Thus it may do so by reacting with either platinic chloride to form chlorplatinic acid or by displacing water in tetrachlorplatinic acid, $H_2PtCl_4(OH)_2$, and thus forming chlorplatinic acid. In chlorplatinic acid, the platinic chloride may be said to serve the same purpose as the water does in the hydrate of hydrogen chloride, that is, it separates the hydrogen and the chlorine of the hydrogen chloride into the two zones. It might be said, therefore, that since water is often spoken of as an ionizing medium for electrolytes, that the platinic chloride is also in the same sense an ionizing medium for certain electrolytes such as hydrogen chloride, potassium chloride, etc.

Since the behavior of ammonia toward hydrogen chloride is similar to that of water and of platinic chloride, it also should yield an acid in forming an ammoniate with hydrogen chloride. This is in fact the case, for when ammonium

chloride or hydrogen chloride is dissolved in liquid ammonia and this solution treated with magnesium or a similar metal, hydrogen is evolved, and the metal is dissolved. At the present time, however, it is not customary to consider such an ammoniate as an acid.

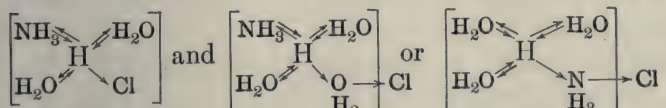
Hydrogen chloride by itself is not an acid, but becomes one when dissolved in water by virtue of the formation of hydrates. In the same way, sulfur trioxide is not an acid and only becomes one when combined with some compound containing hydrogen, such as water. However, sulfuric acid is more closely related in the formulations to the tetrachlorplatinic acid, $H_2PtCl_4(OH)_2$, than to the hydrate of hydrogen chloride. The sulfur trioxide and the platinic chloride first add to the water and then tautomerism and shifting of the hydrogen to the outer zone takes place. On the other hand, with the hydrate of hydrogen chloride, the water first adds and then the chlorine enters the outer zone. Sulfuric acid, $H_2SO_4$, which is itself an addition compound, may add to water to form compounds of the third order such as $H_2SO_4H_2O$; $H_2SO_4.2H_2O$. The constitution of such higher hydrates may be indicated as follows:

$$\left[\begin{matrix} SO_4 \\ (H_2O)_a \end{matrix}\right][H_2 \rightleftarrows (H_2O)_b].$$

It therefore becomes evident that the mono-hydrate, $SO_3.H_2O$, will have the constitutional formula $H_2(SO_4)$ and be similar to tetrachlorplatinic acid $H_2(PtCl_4(OH)_2)$, while the hydrates of the higher orders will have hydrogen in the hydrated form, and correspond to the hydrates of hydrogen chloride.

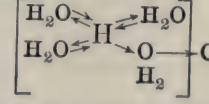
The structures of acids as outlined are not complete for the co-ordination number of the hydrogen has not been taken into account in their development. Unfortunately, the co-ordination number of hydrogen is not known. At the same time, it has not been established experimentally

whether it is necessary for the co-ordination value of a central atom to be satisfied before ionization will take place, or in other words, in order that the compound shall exist in what has been termed inner and outer zones. As far as this point has been investigated, as for platinum, cobalt, and chromium compounds, it seems as if the co-ordination number (maximum) must be satisfied before ionization takes place. With hydrogen chloride and ammonia, for example, ammonium chloride, $NH_4Cl$, would not be an ionogen, but only becomes one when more molecules of ammonia in liquid ammonia solution, or water molecules in an aqueous solution collect about the hydrogen atom until the co-ordination value is reached. If the co-ordination number of hydrogen is assumed to be four, then the formulas for ammonium chloride would be




These formulas involve the view that when ammonium chloride is dissolved in water it undergoes hydration.

The mechanism of the ionization of hydrogen chloride in water may be expressed similarly. The water molecules play the same part as the ammonia forming the hydrate which may be represented as follows:



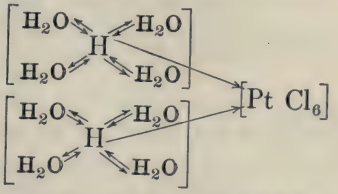

That part of the compound within the brackets or inner zone is the hydrated hydrogen ion. Since water is the common solvent for most electrolytes, it is customary when speaking of hydrated ions to refer to the central atom or group acting as ion, or in this particular case, the hydrated hydrogen ion. When however part of the water molecules

are displaced by ammonia, then they are spoken of as ammonium ion and not hydrogen (or hydrated hydrogen) ion. The similarity is further emphasized by reactions such as the solution of zinc in a water solution of ammonium chloride or the solution of magnesium in a liquid ammonia solution of hydrogen chloride with evolution of hydrogen, similar to the solution of a metal in an aqueous solution of an acid.

It further emphasizes the point that ammonium salts are only hydrogen compounds where the hydrogen atom has associated with one ammonia, while if it has associated with it more ammonia molecules it is generally considered as an abnormal addition compound. Ammonium salts are only one particular case of ammoniated hydrogen compounds. Similarly, oxonium salts are only a particular case of the series of hydrates of hydrogen and similar compounds.

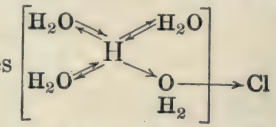
It is also possible by this theory to correlate the fact that platinic chloride dissolved in aqueous hydrochloric acid forms chlorplatinic acid with the formation of addition compounds similar to ammoniates. Since the co-ordination number of the platinum atom is six, the platinic chloride can combine with two molecules of hydrogen chloride to form a compound similar to the diammoniate. Since, however, the addition compound exists in a water solution, the hydrogen chloride can also form the hydrate and equal the co-ordination number of hydrogen. In this case the hydrogen chloride will become ionized just as with the ammonium chloride in the water solution. In other words, either the water or platinic chloride which make up the co-ordination value of the hydrogen of the hydrogen chloride will enter between the hydrogen and the chlorine and separate or ionize them. It is probable that in this case the platinic chloride enters between the hydrogen and the chlorine and hence the structural formula for chlorplatinic

acid may be written as follows—assuming the co-ordination number of hydrogen to be four:




It is to be noted that in the case of chlorplatinic acid the platinic chloride is really considered to be the ionizing agent of the hydrogen chloride, while in the case of the hydrate of hydrogen chloride, water is considered to be the ionizing agent. Furthermore, when platinic chloride acts as the ionizing agent then the hydrogen or hydrated hydrogen occurs in the outer zone or in other words the separate ion, and the chlorine in the inner zone or the complex ion containing the platinum atom. When ammonia or water acts as the ionizing agent in the case of ammonium chloride in a water solution, then the chlorine occurs in the outer zone or in the part which does not remain in the complex ion. If the valence charges upon the various atoms in these addition compounds are taken into account, it also becomes evident that the atom with the same charge as that of the atom which enters in between the two atoms is the one which appears in the outer zone. Thus when the ammonia ionizes the hydrogen chloride the nitrogen is the entering atom and is predominatingly negative and therefore the chlorine would be in the other zone, while when platinum which is predominatingly positive is the entering atom, then the hydrogen which is positive occurs in the other zone from the platinum atom.

It has already been pointed out that hydrogen chloride when dissolved in water acquires the properties of an acid. In the form of its hydrates the maximum co-ordination number of the hydrogen is probably equalled and the water entering between the hydrogen and the chlorine of the

hydrogen chloride causes ionization, which is indicated in the formula by two zones  When platinic chloride is added to an aqueous solution of hydrochloric acid, or hydrate of hydrogen chloride, the dibasic acid chlorplatinic acid is formed, generally given the formula $H_2(PtCl_6)$ and assigned by Werner the structure

$$H_2\begin{bmatrix} Cl & & Cl \\ Cl & Pt & Cl \\ Cl & & Cl \end{bmatrix}.$$

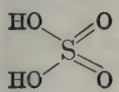
Here again the co-ordination number of hydrogen will be considered as well as that of platinum. In other words, just as in the case of hydrogen chloride in water, the substance does not ionize until the co-ordination value of the hydrogen is reached, and consequently the more correct formulation would be $(H_2O\rightleftarrows)_xH_2[PtCl_6]$. The part actually played by the platinic chloride in forming the chlorplatinic acid in a water solution of hydrogen chloride, is that platinic chloride replaces the ionizing molecule of water in the hydrate of hydrochloric acid.

$$\left[(H_2O\rightleftarrows)_x\,H{-}\overset{H_2}{O}\right]Cl + Pt\,Cl_4 \gg\longrightarrow (H_2O\rightleftarrows)_xH_2{=}\left[\overset{Cl_4}{Pt}{=}Cl_2\right]$$

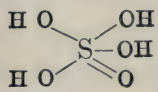
It is interesting to note the frequency of the occurrence of complexes in the inner zone in which the co-ordination number of the central atom is eight. $H_2(SO_4)$, $H(MnO_4)$, $H(ClO_4)$, $H_3(AsO_4)$, $(RuO_4)$, $(OsO_4)$, etc., all conform to the general type $(AO_4)$ for the inner zone, water of hydration being omitted in these formulas. In determining the co-ordination number of an atom, the rule is followed here that a univalent atom such as chlorine and a compound such as hydrogen chloride counts as one, while a bivalent atom such as oxygen counts as two. This rule is arbitrary.

For the present it is necessary to have some such rule and collect data. It will undoubtedly be possible in the future to find a more general rule and method of determining these capacity numbers.

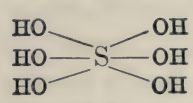
It was stated before that it has been customary to assign the hydroxyl structure to sulfuric acid and its hydrates.




$SO_3.H_2O$

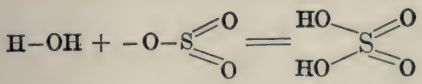



$SO_3.2H_2O$




$SO_3.3H_2O$

According to these structures the double linking between the oxygen and the sulfur opened up and added the hydrogen and hydroxyl of the water, forming in this way two hydroxyl groups combined with the sulfur in place of one oxygen




Accordingly, the dihydrate should be a tetrabasic acid if the acidity were due to the hydrogen of the hydroxyl, but this is contrary to experimental facts. Similarly, osmium and ruthenium oxides might be expected to show a greater tendency to form acids than sulfur trioxide since they contain more oxygen atoms with double linking to combine with the water. It is evident, therefore, that a knowledge of the co-ordination number as well as of the atomic valence is necessary in order to determine the basicity of an acid.

Just as there is a series of acids in which the co-ordination number of the central atom is eight, a series of acids exists in which the co-ordination number is six. An example of this series is nitric acid $H(NO_3)$. The atomic valence of the nitrogen is plus five, the co-ordination number six, and the basicity one. The same is true of chloric acid $H(ClO_3)$, iodic acid $H(IO_3)$, etc. Meta-phosphoric acid, $H(PO_3)$, belongs to this group, although ortho-phosphoric

acid, $H_3PO_4$, belongs to the group in which the co-ordinatio number is eight. This brings up the question of whethe an acid, the co-ordination number of whose central atom i six, can be converted into one whose central atom has a co-ordination number of eight by means of hydration This appears to be possible, for example, in passing from metaphosphoric acid to the ortho acid. On the other hand nitric acid, and the nitrates of the alkali metals, form hydrates, but only mono-basic nitric acid has been observed experimentally. The additional molecules of water in the hydrates of nitric acid may, therefore, be combined with the hydrogen atom which would act as a second central atom, or be combined with the nitrogen in such a way as not to tautomerize the hydrogen of these water molecules into the outer zone, or they may be added to the double linking between the oxygen and nitrogen and be present as hydroxyl groups.

$$\left[(H_2O)_n \rightleftarrows H\right]\left[NO_3\right] \quad \text{or} \quad H\left[NO_3 \rightleftarrows (H_2O)\right] \quad \text{or} \quad H\left[\begin{matrix} O & & OH \\ & \diagdown\ \diagup & \\ & N & \\ & \diagup\ \diagdown & \\ O & & OH \end{matrix}\right]$$

The co-ordination number is a function of external physical conditions. Its value in the case of the nitrogen in nitric acid is six in all the conditions under which nitrates have been studied. With the acids of phosphorus, however, the co-ordination number may change from six to eight. This change is similar to the changes which occur with atomic valence. Some elements can show several different states of valence, while others show only one.

The ionic theory showed that bases yield hydroxyl ions in aqueous solution, and that a base might be defined as a substance which in solution forms hydroxyl ions.

Since ammonium salts can be formed directly by the addition of ammonia and acid to each other, ammonia itself has sometimes been spoken of as a base. Similarly, since amines are like ammonia in this respect, they also

have been considered to be bases. At first, in order to distinguish them from the true metallic alkalies, they were sometimes called alkaloids (A. W. Hofmann, Lieb. Ann. *73*, 91 (1850)). This term, however, is now reserved for the more complicated amines which occur in nature, which show marked physiological properties. Two different definitions for the term base have been current with the amines. (1) They furnish hydroxide ion in aqueous solution. (2) They combine with acids to form substituted ammonium salts. This, naturally, has led to some confusion, since amines have frequently been called strong bases or weak bases, depending upon the amount to which ammonium salts were formed when they were added to an acid.

According to the ionic theory, the relative strengths of different bases are given by the ionization constants as calculated from the Ostwald dilution law, these depending upon the concentrations of ionized and un-ionized substances present in solution. The equation for calculating the ionization constant (which naturally should hold for all substances in solution, not merely bases) is as follows for a substance BA, ionizing into $B^+$ and $A^-$:

$$\frac{[B^+][A^-]}{[BA]} = K,$$

in which the terms in brackets denote the concentrations.

Highly ionized substances, including the bases sodium and potassium hydroxides, etc., give values for the ionization constants which vary with the concentration. On the other hand, slightly ionized bases, among which may be included some of the substituted ammonium hydroxides, give constant values, and it appears as if the strengths of these bases might be compared in this way. A difficulty arises, however, which prevents a direct comparison. Distribution experiments with organic solvents and an aqueous solution of ammonia, showed that in the water only a part

of the latter was present as ammonium hydroxide, the rest being dissolved as such (ammonia) or more probably as a hydrate. The ionization constant, to show the strength of the base should be calculated from the concentration of the ammonium hydroxide from the equation

$$\frac{[NH_4^+][OH^-]}{[NH_4OH]} = K_1.$$

At the same time, the equilibrium

$$\frac{[NH_3][H_2O]}{[NH_4OH]} = K_2,$$

or some similar equilibrium, must be taken into account. The same is true for the substituted ammonium hydroxides. The values of the ionization constants for these bases, as determined ordinarily, are apt to be misleading for this reason. A few of the values have been determined correctly. The influence of the solvent is shown here, but a satisfactory interpretation of its action in the ionization of these bases and of other bases is not given in the ionic theory. The further developments, just as with the acids, follow the lines indicated by Werner and the conceptions developed here.

According to Werner (Neuere Anschauungen, pp. 268–270), an anhydro base is a substance which forms a hydrate with water and then yields hydroxide ion and a complex positive ion in aqueous solution. The anhydro base ionizes in this way by combining with the hydrogen ion of the water, and producing hydroxide ions (from the water) in a concentration characteristic for the substance. Aquo bases, or bases, are addition compounds of substances with water which yield hydroxide ions in aqueous solution. The method of indicating these relations with hydroxyl in the outer zone, etc., follows from what has been said before. The introduction of the electron conception of valence shows the distribution of the charges, etc. It will not be necessary to develop these relations further here.

The statement is sometimes made that tetramethyl ammonium hydroxide is so strong a base that neither sodium nor potassium hydroxide can separate it from its salts, but that silver hydroxide must be used for this purpose. It is much more probable that the reason for the silver hydroxide being much more efficient than the alkali hydroxide is the low solubility of the silver halide usually formed as one of the dissociation products of the intermediate addition compound. In place of using silver hydroxide, the same reaction may be brought about by allowing the reaction to take place in some other solvent such as alcohol. This is a way of changing the external physical conditions so as to favor the dissociation of the intermediate addition compound in the desired direction as will be explained in later chapters, because of the smaller solubility of the sodium or potassium chloride in alcohol.

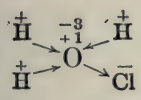
The state of substances in solution will now be taken up briefly. The electrolytic dissociation of a large number of substances is dependent evidently upon the properties of the solvent as well as upon the character of the dissolved substance (solute), because on the one hand all substances do not ionize in a solvent such as water, and on the other hand, a substance may ionize in one solvent, hydrogen chloride in water, and not in a different solvent, hydrogen chloride in benzene. The solvent must, therefore, also be considered in the ionization relationships and the manner in which it may be done follows directly from what has been said.

As pointed out, hydrogen chloride in itself is not an acid, but only becomes one when it forms a compound of a higher order, or in other words, an addition compound. Hydrogen chloride is able to form compounds of higher orders with the compounds of the first order, ammonia, platinic chloride, sulfur trioxide, auric chloride, water, etc., the compounds of the second order which are formed being

formulated as follows: $[HNH_3]Cl$, $H_2[PtCl_6]$, $H[SO_3Cl]$, $H[AuCl_4]$, $[H_2OH]Cl$, etc. The linkings between the individual atoms, however, follow the principles outlined in the first chapter, the division of the compounds into zones as a rule not influencing the distribution of the electric charges due to the combinations between the atoms, except for some cases of intramolecular oxidation and reduction.

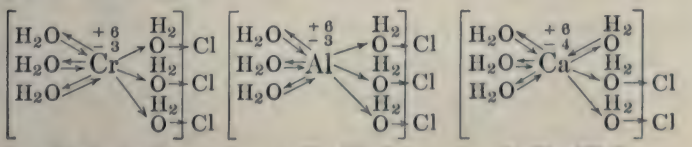
The last of the compounds given in the preceding paragraph was $[H_2OH]Cl$. This compound with water would evidently be an example of the compounds formed when hydrogen chloride is dissolved in water. Many substances combine with water to form compounds containing water of crystallization. In the last fifteen years much evidence has been accumulated which shows that hydrates exist in solution as well, and also that ions are hydrated. The most careful work in this field was done by E. W. Washburn and by G. Buchböck, the former studying the relative hydration of the positive and negative ions of the chlorides of lithium, sodium, potassium, and caesium, and the latter of hydrochloric acid. That is to say, they determined the ratio between the number of water molecules combined with the lithium, sodium, potassium, cæsium, or hydrogen ion, and the number of water molecules combined with the negative chlorine ion for certain definite concentrations of aqueous solutions of these salts. Different amounts of water were found to be combined with the positive ions, but in every case, more water was combined with or associated with, the positive ion than with the negative ion. It was impossible to determine directly whether any water was associated with the negative ion, since the method permitted only of the determination of the relative extents of hydration.

The existence of hydrated ions rests therefore upon a firm experimental basis. The formula for the compound hydrogen chloride with water was given as $[H_2OH]Cl$. In detail

this would be  in which the oxygen is in the onium state with a valence of $-3+1=-2$. The predominatingly negative oxygen holds the positive hydrogen in the inner zone and the negative chlorine in the outer zone, and the ions are $[H_3O]^+$ and $Cl^-$, omitting the additional water molecules which may be combined with the hydrogen and the chlorine.

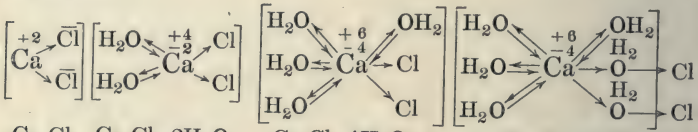
It is necessary to mention here the fact that water may also be in combination with, or associated with the negative ion, as well as with the positive ion. A salt such as hydrated magnesium sulfate will illustrate this. The composition of this substance is $MgSO_4.7H_2O$. It has been shown by vapor tension measurements that six of the water molecules bear the same relation to the molecule as a whole, but different from the seventh molecule. Furthermore, the study of the optical activity (rotation of the plane of polarized light) of the substance, indicates that one molecule of water is associated with the $SO_4$ group. This indicates that the water may be present in combination with either of the two parts of the molecule which form the ions, or that both positive and negative ions may be hydrated.

It was shown previously that hydrates and ammoniates belong to the class of addition compounds. The substance $CrCl_3.6H_2O$, for example, is similar in structure to the substance $PtCl_4.6NH_3$, etc. The water in these compounds is in combination with the metallic atom in the inner zone or sphere, where the latter functions as the central atom. The structures of some of these compounds may therefore be given as follows:



$Cr\,Cl_3.6H_2O$ $Al\,Cl_3.6H_2O$ $Ca\,Cl_2.6H_2O$

It was pointed out that the co-ordination number of the central atom varied, depending upon certain physical conditions such as temperature, etc. This means that the number of molecules of water in the hydrated salts varies with the conditions, but there are certain limits within which a hydrated salt having a perfectly definite composition is stable. A study of these substances from the point of view of the phase rule shows the compositions and ranges of stability of the various hydrates and other compounds. For calcium chloride, the forms which are known include $CaCl_2$, $CaCl_2.2H_2O$, $CaCl_2.4H_2O$, and $CaCl_2.6H_2O$. The graphic formulas for these substances might be written as follows:



$Ca\,Cl_2$ $Ca\,Cl_2.2H_2O$ $Ca\,Cl_2.4H_2O$ $Ca\,Cl_2.6H_2O$

Several relations are brought out by these formulas In the first place, the calcium is taken to be in the same state of oxidation (+ 2) in all the compounds. In the second place, according to these formulas, the only substance which would ionize in solution is the last which would form the ions $[Ca.6H_2O]^{++}$ and $2\bar{C}l$. At present there is no experimental evidence available to test this question, and the reason for writing the formulas in this way and indicating this fact is that with similar compounds, such as the hydrates of chromic chloride and the ammoniates of platinic chloride, the chlorine only appears in the outer zone and forms ions when the final hexahydrate or hexammine stage is reached. For this reason the di- and tetrahydrates are formulated as non-ionogens.

It has been possible so far to assign definite structural formulas to many of the compounds which are made up of two or more simpler molecules (compounds of the second

and higher orders). The formulas assigned have been based upon certain definite chemical and physical reactions or relations. The compounds have a fairly considerable range of stability so that the study of their reactions makes it possible to treat of a portion of the molecule at a time, leaving the remainder constant or unchanged. In developing the subject, it is now necessary to take up more complex substances; that is to say, the compounds of the second, third, etc., order, or the binary, ternary, etc., compounds. These compounds of higher orders are made up of compounds of the first order, and must be considered in the same way as far as possible. A difficulty is encountered in the practical treatment. That definite compounds are formed may be proved conclusively in many of these binary or ternary mixtures, but the linkings between the atoms cannot be determined as definitely. The methods in use for determining the graphic formulas cannot be applied to these more complex substances, partly because of their ready dissociation into their constituent molecules, partly because of the internal rearrangements which take place readily, and perhaps for other reasons. The difficulty of assigning definite structural formulas to a number of these substances must be faced squarely. An attempt to write the formulas with insufficient evidence is of no value, but on the other hand it is possible to use the classifications involving these compounds of higher orders without assigning graphic formulas to them. In a way this appears to go no further than to designate these compounds as molecular compounds, but it will be shown in succeeding chapters how different classes of reactions may be grouped together so that even without the use of all the linkings between the atoms, light will be thrown upon the mechanism of a number of reactions. This is true especially when the distribution of the charges on the atoms constituting the molecules is taken into account.

## CHAPTER IV.

### CATALYSIS.

THE conceptions upon which the structures of molecules are based have been elaborated in the preceding chapters. The next step to be taken involves the changes which may take place when two or more molecules interact. This would include changes which take place in chemical reactions and an attempt will be made to outline a general theory of chemical reactions from the standpoint of structural chemistry in this and the following chapters.

In considering such a general theory of chemical reactions, it is desirable to proceed from simple to more complex phenomena. In order to lead up to chemical reactions in general, catalytic reactions will first be taken up as simple examples. This apparently reverses the customary order of treatment, but a short discussion of catalysis as it is ordinarily presented and as it will be presented here will serve to show the relations.

A catalytic action is generally defined as one in which the velocity of a reaction is modified by the presence of a substance which is itself unchanged at the end of the reaction. The substance which causes such an action is called the catalytic agent or catalyst. The following general relations have heretofore been assumed to apply to catalytic actions.

In the first place, the catalyst has the same chemical composition at the beginning and at the end of the reaction. A small amount of the catalyst is able to effect the transformation of a large amount of the reacting substance. A catalyst can only modify the velocity of a reaction, it is incapable of starting a reaction. A catalytic agent does not affect the final state of equilibrium of a reaction, or, in other words, the velocities of two opposing

reactions are affected to the same extent by the catalyst. The state of equilibrium is independent of the nature and quantity of the catalytic agent.

These general relations have been taken to hold for catalytic actions as a result of the description of various reactions. They are therefore, used as definitions of catalytic reactions. If, by definition, a reaction follows these laws, it is catalytic, otherwise it is not. While it is necessary for purposes of classification, to have some definitions of this kind, the way in which the classification of catalytic reactions developed, that is, very often by the introduction of the term catalyst when unknown factors were involved, has confused the relation of these reactions to chemical reactions in general.

In place of the relations pointed out, a catalytic action will be taken to be based upon the definition of a catalyst as a substance which may modify the velocity of a reaction without itself undergoing a change in chemical composition. No further limitations will be introduced, and it will be shown how the conclusions from this point of view compare with the conclusions derived from or based upon the description of catalytic reactions used heretofore. The definition given when used with the general equation of a chemical reaction evidently simplifies it from the structural or compositional point of view, because the chemical composition of one of the initial and final products of the reaction is the same. The way in which such a substance may modify the velocity of a reaction must next be considered, and it is this point which forms the crux of the general theory to be used. The general theory consists of what has been called the "addition theory" of chemical reactions.

In considering the mechanism of chemical reactions, this theory states that primary addition is involved in chemical reactions between molecules even when the final products obtained indicate substitution or other change. It repre-

sents the most general case of chemical reactions. Evidence for an explanation for a number of reactions on this basis and the view that it was of general application was presented some years ago in a short paper (K. G. Falk and J. M. Nelson, Jour. Amer. Chem. Soc. *37*, 1732 (1915)). Catalytic reactions will be taken up as a group of addition reactions following the same laws as other chemical reactions, with one condition fixed, namely, that one of the original substances which takes part in the reaction also appears as one of the products of the reaction. The complete change may be represented by an equation of the form,

$$A + B + \cdots + D = E + F + \cdots + D,$$

in which the substance typified by $D$ acts as the catalyst. A reaction such as this may be considered to proceed by an addition compound being formed by the reacting components with the catalyst, and this complex compound then reacts further to reform the catalyst and one or more new molecules. The proviso for a reaction to be considered catalytic is that one of the substances going to make up the addition product is formed again when the addition product breaks down or reacts further. This substance, the catalyst, which has gone through a cycle of changes and has returned to its original condition, is evidently able to go through the cycle of changes again with fresh material. The action of the catalytic substance, as outlined, may result in an acceleration of the changes taking place in the other substances present, a retardation, or finally show no effect on the velocity of the reaction. If a retardation would result when the catalyst takes part in the reaction, then, since reactions would be taking place simultaneously without and with the catalytic substance as part of the intermediate addition compound, the net result observed with regard to the velocity would be that in which the catalytic substance was not involved unless the latter

were present in more than a very small quantity. The experimental evidence directly in favor of the view of the production of addition compounds in a number of catalytic reactions will be considered next and then some theoretical developments will be given.

In the lead chamber process for the manufacture of sulfuric acid, nitric oxide, oxygen (from the air), sulfur dioxide, and water (steam), interact. The nitric oxide acts as the catalyst, and is present at the end of the action, with the sulfuric acid. It acts as "oxygen carrier." One of the intermediate compounds which is formed contains nitrogen peroxide ($NO_2$), sulfur dioxide, and water. It may be obtained in crystalline form, known as "chamber crystals" which have the composition $HSO_3NO_2$, nitrosulfonic acid, under certain conditions. This substance is decomposed in the presence of an excess of steam or water vapor into sulfuric acid and nitric oxide, or better, nitrogen trioxide, $N_2O_3$. While the exact formulation of the intermediate compounds is not simple under the various conditions, the evidence at hand is sufficient to make the existence of at least one intermediate compound certain.

The reaction between an alcohol and an acid to form an ester, catalyzed by the addition of acid, takes place with the formation of a complex intermediate compound containing the catalyst as a constituent. The evidence for this and a more complete discussion of this reaction will be presented in Chapter 6. The existence of such intermediate compounds is only referred to here, because they have been shown definitely to exist in a number of cases.

In the formation of ether and water, or of ethylene and water from alcohol and sulfuric acid, or the reverse reactions, sulfuric acid plays the part of the catalyst, and the intermediate addition compound may be represented by alkyl sulfuric acid, $RSO_4H$, or a hydrate of it.

Similarly in the formation of ethylene and water from

ethyl alcohol, zinc chloride acts as catalyst, and the intermediate compound is represented by the formula $ZnCl_2.C_2H_5OH$.

Condensation reactions with aluminium chloride as catalyst also involve the formation of intermediate complex compounds which have been isolated in some cases. These will be taken up in detail in Chapter VII.

The catalytic reactions which have been quoted give direct experimental evidence of the existence of intermediate compounds of the reacting substances with the catalyst. The list as given is not complete by any means, and a study of the scientific and patent literature of the past few years will show many more reactions of this kind. P. Sabatier, in his book "La Catalyse en Chimie Organique," 1913, assumed the formation of an intermediate compound of catalyst with reacting substances in all catalytic reactions. The fact that intermediate compounds have been isolated shows that a capacity for combination, or, in other words, an unsaturation, is present in the reacting substances. This unsaturation may depend upon a definite atom of each molecule, or upon a group of atoms combined in such a way as to show unsaturation of two or more atoms (as, for example, with two carbon atoms united by a double linking or two units of valence), but in all cases, the important feature at present is the property of unsaturation in connection with the formation of the intermediate compound.

The fact that intermediate complex compounds have been isolated in a number of catalytic reactions, naturally does not prove that they are formed (with the catalyst) in all such cases. Some evidence will now be presented to indicate that unsaturation of certain molecules plays an important part in catalytic reactions which apparently do not, at first sight, fall into the classification.

It has been known for some time that a given reaction

may proceed faster in one solvent than in another. As an example, the reaction between triethylamine and ethyl iodide in which tetraethylammonium iodide is formed, and for which the rate in different solvents was studied by N. Menschutkin, may be quoted. Menschutkin mixed one volume of equimolecular amounts of the reacting substances with fifteen volumes of the solvent, and heated the mixtures in sealed glass tubes at 100° for definite periods of time.

*Velocity of Combination of Triethylamine with Ethyl Iodide in Various Solvents.*

| | Velocity Constants. | Ratios. | |
|---|---|---|---|
| **Hydrocarbons.** | | | |
| Hexane $C_6H_{14}$ | 0.000180 | 1 | 0.13 |
| Heptane $C_7H_{16}$ | 0.000235 | 1.3 | 0.17 |
| Xylene $C_6H_4(CH_3)_2$ | 0.00287 | 15.9 | 2.2 |
| Benzene $C_6H_6$ | 0.00584 | 38.2 | 4.4 |
| **Halogen compounds.** | | | |
| Propylchloride $C_3H_7Cl$ | 0.00540 | 30 | 4.0 |
| Phenylchloride $C_6H_5Cl$ | 0.0231 | 128 | 17.4 |
| Phenyl bromide $C_6H_5Br$ | 0.0270 | 150 | 20.3 |
| $\alpha$ Bromnaphthalene $C_{10}H_7Br$ | 0.1129 | 627 | 84.9 |
| **Simple Ethers.** | | | |
| Ethyl isoamyl ether $C_2H_5OC_5H_{11}$ | 0.000630 | 3.5 | 0.47 |
| Ethyl ether $C_2H_5OC_2H_5$ | 0.000757 | 4.2 | 0.57 |
| Phenetol $C_2H_5OC_6H_5$ | 0.0212 | 117.7 | 16.0 |
| Anisol $CH_3OC_6H_5$ | 0.0403 | 223.9 | 30.3 |
| **Esters.** | | | |
| Isobutyl acetate $C_4H_9.O.CO.CH_3$ | 0.00577 | 32.1 | 4.3 |
| Ethyl acetate $C_2H_5O.CO.CH_3$ | 0.0223 | 123.9 | 16.7 |
| Ethyl benzoate $C_2H_5O.CO.C_6H_5$ | 0.0259 | 143.9 | 19.4 |
| **Alcohols.** | | | |
| Isobutyl alcohol $C_4H_9.OH$ | 0.0258 | 143.3 | 19.4 |
| Ethyl alcohol $C_2H_5.OH$ | 0.0366 | 203.3 | 27.5 |
| Allyl alcohol $C_3H_5.OH$ | 0.0433 | 240.5 | 32.5 |
| Methyl alcohol $CH_3.OH$ | 0.0516 | 286.6 | 38.0 |
| Benzyl alcohol $C_6H_5.CH_2.OH$ | 0.133 | 742.2 | 100.0 |
| **Ketones.** | | | |
| Acetone $CH_3.CO.CH_3$ | 0.0608 | 337.7 | 45.7 |
| Acetone (14.5 vol.) + Water (0.5 vol.) | 0.0889 | 493.9 | 66.9 |
| Acetophenone $CH_3.CO.C_6H_5$ | 0.1294 | 718.7 | 97.3 |

The determination of the amounts of tetraethylammonium iodide formed, enabled him to calculate the velocity constants for the reaction using the equation for a bimolecular reaction. Some of these values ($k$) for the reaction in different solvents are given in the accompanying table [Z. physik. Chem. *6*, 43 (1890)]. The ratios given in the last two columns show the relative rates of reaction, first when compared to the slowest reaction, whose velocity is placed equal to one, and second, on the basis of the most rapid reaction which is placed equal to 100.

The results given in this table do not indicate clearly that the velocity is directly connected with the unsaturation as ordinarily considered. Roughly it is so, and if certain solvents are omitted, this relation is very nearly true. For the present, it may be stated that the unsaturation is important in that it shows the capacity to form addition products, but that in some of the solvents, polymerization of the solvent molecules themselves occurs. The unsaturation shows itself in two ways, as polymerization and as formation of complex molecules with other substances, and the action of the solvent is determined by these two factors and their relative predominance.

It may be said for the present, therefore, that a rough parallelism between the unsaturation of the solvent and the magnitude of the velocity constants for this reaction exists.

Unsaturation may therefore be used as the property upon which the catalysis of these reactions depend. Without entering into the structural formulas of the addition products at present, this property means that addition compound formation of one or all of the reacting substances with the catalyst precedes or accompanies the reactions. D. Klein [Jour. Phys. Chem. *15*, 1 (1911)] in studying the relative rates of the reaction between hydrogen sulfide and sulfur dioxide in a number of organic substances,

accounted for the results obtained by the assumption of intermediate compounds involving the reacting compounds and the solvents as catalysts. The evidence in other reactions is also strong enough to have caused a number of workers to assume the existence of such intermediate products, without actually having isolated them. Some of these reactions are given by J. W. Mellor in his "Chemical Statics and Dynamics."

The theoretical views of E. C. C. Baly, based upon the absorption in the ultraviolet region of the spectrum of the reacting substances, before, during, and after the reaction, and outlined in Chapter II may be referred to in this connection.

A group of catalytic agents which is continually increasing in importance is included under the general term of enzymes, the catalysts produced by living organisms and which are of the greatest significance in all life processes. Within recent years there have been distinct advances made in the elucidation of the chemical nature of some of the enzymes, but there is no definite evidence at the present time that any has been obtained in a pure state, that is, as a definite chemical compound. Notwithstanding this lack of knowledge, a study of the kinetics of a number of enzyme reactions has led to the view that primary addition products are formed between the enzyme molecule and the substrate (substance acted upon) and that the addition products then react further to reform the enzymes and the other products of the reactions. One of the lines of evidence for this view may be indicated briefly. With a small amount of enzyme material, increasing the amount of substrate will at first, with small quantities of the latter, show a larger amount of decomposition in a given time interval, up to a certain amount of substrate. Increasing the concentration of substrate beyond this will result in the same amount of action as with the smaller amounts, evidence that the

given quantity of enzyme can take care of only a certain quantity of substrate, or that a compound of the two is formed. The possible question of adsorption will be taken up presently. Another way of stating the same observation is that with small amounts of enzyme, the amount of substrate transformed in a given time interval is proportional to the length of the time interval. Among others, this was found to be true for the action of invertase on cane sugar by J. M. Nelson and W. C. Vosburgh (Jour. Am. Chem. Soc. *39*, 790 (1917)), by J. Duclaux [Chemie Biologique, Paris, 1883; and Traité de Microbiologie, Tome II, Diastases, Toxines, et Venims, Paris, 1899], by A. Brown (Trans. London Chem. Soc. *81*, 373 (1902)] and by L. Michaelis and M. L. Menten (Biochem. Z. *49*, 333 (1913)); of amylase on starch by H. T. Brown and T. A. Glendinning [Trans. London Chem. Soc., *81*, 388 (1902)]; of the action of lactase, maltase, and emulsin by E. F. Armstrong [Proc. Roy. Soc. *73*, 500 (1904)]; of lipase on glyceryl triacetate by K. G. Falk and K. Sugiura [Jour. Amer. Chem. Soc. *37*, 227 (1915)] and of urease on urea by D. D. van Slyke and G. E. Cullen [Jour. Biol. Chem. *19*, 141 (1914)]. The well-known lock and key simile of Emil Fischer for such reactions indicates also a belief in a chemical combination as the first step. H. D. Dakin [Jour. of Physiol. *30*, 253 (1904)] found evidence for the existence of intermediate compounds in the action of optically active liver lipase material on a racemic mixture of esters of mandelic acid, the dextro-component reacting more rapidly than the lævo. "The dextro- and lævo-components of the inactive ester first combine with the enzyme, but the latter is assumed to be an optically active asymmetric substance, so that the rates of combination of the enzyme with the d- and l-esters are different. The second stage in the reaction consists in the hydrolysis of the complex molecule (enzyme + ester). Since the complex molecule (enzyme + d-ester) would not

be the optical opposite of (enzyme + l-ester), the rate of change in the two cases would again be different. Judging by analogy with other reactions one might anticipate that the complex molecule which is formed with the greater velocity would be more rapidly decomposed. In the present case, it would appear that the dextro-component of the inactive mandelic ester combines more readily with the enzyme than the lævo-component does, and that the complex molecules (d-ester + enzyme) are hydrolyzed more rapidly than the (l-ester + enzyme), so that if hydrolysis be incomplete dextro-acid is found in solution and the residual ester is lævo-rotatory."

The views so far presented in this chapter may be summarized as being based upon the primary formation of addition compounds when two or more molecules react, these addition compounds then breaking down to form new molecules. In catalytic reactions, the first stage of the reaction is the same, but in the second stage, one of the substances formed in the breaking down of the intermediate compound is identical in composition with one of the substances which took part initially in the reaction in the formation of the addition compound. While the experimental evidence is favorable to this view of catalytic reactions in many cases, it may be objected that physical influences may often modify the velocity of the reaction between gases. At present there is no experimental evidence of any kind available to prove or disprove the formation of definite chemical compounds in such cases, but on the other hand, evidence is accumulating that adsorption (or perhaps the solution of a gas or a liquid in a solid) is the important factor here. Just how far phenomena of this nature may be identical with the formation of definite chemical compounds (possibly so-called "loose" combinations) on a surface is not at present certain, but until direct evidence is obtained that such reactions must be included in a

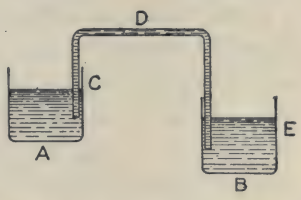
scheme different from the one outlined here, the present classification may be used to include all these reactions, although the composition, and even in many cases the nature, of the intermediate compounds, is not known.

The reactions between two or more molecules take place with the formation of intermediate compounds. For the sake of completeness, it will be necessary to refer to the reactions in which one substance only is changing or reacting. This substance may be a simple molecule reacting, or may be a molecule of a complex intermediate addition compound, made up of two or more simpler molecules. The rate of such reactions appears to depend entirely upon the nature of the substance, and while it is influenced by the temperature, a certain fraction of the amount present is transformed in each unit of time, the monomolecular reaction velocity rate, or the logarithmic law, being followed. A number of theories have been suggested to account for the fact that only such a part reacts, and not the whole amount, such as an attempt to distinguish between active and inactive molecules of a substance, of which only the former react, while a constant ratio exists between the concentrations of the two kinds. None of these theories has been satisfactory, and for the present at least it is advisable simply to state the fact without attempting to explain it.

Some theoretical relations with regard to catalytic reactions will now be taken up. A simple mechanical analogy developed by Professor J. M. Nelson and Dr. J. H. Northrop, may be of interest here in considering the energy or affinity relationships, although it does not include the view of addition compound formation.

A vessel of water, $A$, is filled to the level $C$. A syphon, $D$, filled with water dips into this water, while its other, lower, end reaches to the vessel $B$ placed lower than $A$, so that the level of the water in $B$ ($E$) at the beginning is

higher than the bottom of vessel *A*. The water will flow from vessel *A* into vessel *B* until the levels in the two are the same. In this analogy, the substances initially are represented by the water in *A*, the substances after the reaction by the water in *B*, the difference in the content of free energy is shown by the difference in level in the two vessels. The change of the substances from vessel or state *A* to vessel or state *B* of lower free energy content takes place through the syphon, and may occur in a number of ways, depending upon the syphon. Change takes place until equilibrium is reached, and the rate of change depends upon the bore, etc., of the syphon, which includes therefore the catalytic influences. The raising of the water in the left arm of the syphon may represent the work necessary to overcome the chemical resistance, this work being regained in the other arm of the syphon. The catalytic properties of the syphon remain, after the reaction, the same as before, and the reaction would proceed, even if the bore of the tube were infinitesimal, but at an infinitesimal rate.




The general conditions which had been assumed to hold for catalytic reactions and which were used to determine whether a substance acted as catalyst, were given earlier in this chapter. They were evolved gradually as more and more reactions of this nature were studied, and it is not surprising therefore that this superstructure of conditions became top-heavy and that some of the conditions assumed to be essential in a catalytic reaction, at times were found not to hold. The question whether the equilibrium point of a reaction is changed by a catalyst is a case in point. If a catalyst only changes the velocity of a reaction, and exerts no other influence whatsoever, as assumed in the

customary statement of catalytic changes, then the catalyst cannot change the equilibrium of the reaction; otherwise perpetual motion would be possible.

From time to time statements have appeared in the literature taking exception to the view that a catalyst does not change the equilibrium, without, however, going to the root of the question and attempting a classification and description of catalytic actions which would eliminate such contradictions. Thus, G. Bredig (Ergebnisse der Physiologie I, *139* (1902)) showed that a change in the vapor pressure of a catalyst necessitates a difference in the work required to remove the catalyst from the reaction mixture. Only as long as this work is the same under the same conditions before and after the reaction, does the equilibrium remain unchanged. If the catalyst is present in large excess it acts as solvent. A change in the nature of the solvent changes the equilibrium, and only in dilute solution will the equilibrium remain the same. E. Abel [Z. Elektrochem. *13*, 555 (1907)] stated, assuming the formation of intermediate products with the catalyst, that if the catalyst is in a different chemical or physical state at the end of the reaction from what it was at the beginning, that it has given up or received energy, and that a change in the equilibrium was quite conceivable. W. J. Jones and A. Lapworth [Trans. London Chem. Soc. *99*, 917 (1911) found experimental evidence for the change in the equilibrium between ethyl alcohol, acetic acid, ethyl acetate, and water, by the addition of the catalyst hydrogen chloride. M. A. Rosanoff (Jour. Amer. Chem. Soc. *35*, 173 (1913)) also speaks of the possibility of a catalyst influencing the equilibrium, and that it does not do so only when the molecular state of the reagents is not affected by the catalyst. A number of other chemists may be quoted in the same sense. Recently, W. D. Bancroft (Jour. Physical Chemistry *21*, 573 (1917)) reviewed certain phases of catalytic reactions and took up some of the questions discussed here.

If a catalytic reaction is defined as a reaction in which one of the products is identical in chemical composition with one of the original substances involved in the reaction, the view which is used here, then it may be possible to arrive at definite general conclusions. No further limitations are introduced in the definition. In the general formulation of a chemical reaction:

$$V_1\alpha_1 + V_2\alpha_2 + \cdots n_1A_1 + n_2A_2 + \cdots$$
$$= V_1'\alpha_1' + V_2'\alpha_2' + \cdots n_1'A_1' + n_2'A_2' + \cdots$$

in which $\alpha_1\alpha_2, \cdots \alpha_1^1, \alpha_2^1, \cdots$ represent the molecular species in the solid state taking part in the reaction, $A_1, A_2, \cdots A_1', A_2', \cdots$ the molecular species either as gas or in solution, and $V_1, V_2, \cdots n_1, n_2, \cdots V_1', V_2', \cdots n_1', n_2', \cdots$ the corresponding molecular species formed in the reaction, then the definition of catalytic action advanced requires only that one of the molecular species $\alpha_1', \alpha_2', \cdots A_1', A_2', \cdots$ is identical in composition with $\alpha_1, \alpha_2, \cdots A_1, A_2, \cdots$. The definition does not, *a priori*, state anything concerning the velocity of the reaction. Since one of the substances appears as a product of the reaction, obviously it may go through the cycle of the reaction again with fresh initial material. This substance is the catalyst, and therefore a small amount of this substance may react with a large amount of the other substances. This phenomenon has always been taken to be one of the most characteristic properties of a catalyst. With regard to the possibility of the reaction taking place in the absence of the catalytic substance, if everyone of the substances at the beginning and at the end of the reaction is present in the pure state, then the equilibrium constant derived from the law of mass action would be independent of the catalytic substances, the equilibrium would be the same whether the catalyst were present or not, and reaction would proceed in the presence

or absence of catalyst, although the rates in the different cases may well be different. Furthermore, it is impossible to state the effect of the catalyst; it might increase the rate of the reaction, it might decrease it, or it is possible that no effect at all would be noticeable upon the rate of the reaction. The so-called "negative catalysis" (cf. Mellor, l.c.) is then simply a special case of catalysis in general, the catalyst here retarding the reaction instead of accelerating it.

In practical work, the substances taking part in a reaction are hardly ever isolated in a pure state, so that a development of the ideal case just presented will be necessary. If, in the general formulation of a chemical reaction given above, the concentrations of the substances $A_1$, $A_2$, $\cdots$ $A_1'$, $A_2'$, $\cdots$ in the free state before and after the reaction are denoted by $C_1$, $C_2$, $\cdots$ $C_1'$, $C_2'$, $\cdots$ and their concentrations at equilibrium by $c_1'$, $c_2'$, $\cdots$, then it may readily be shown that the change in the free energy ($A$) of the reaction is given by the equation,

$$A = RT \log_e \frac{C_1^{n_1} C_2^{n_2} \cdots}{C_1'^{n_1'} C_2'^{n_2'} \cdots} - RT \log_e \frac{c_1^{n_1} c_2^{n_2} \cdots}{c_1'^{n_1'} c_2'^{n_2'} \cdots}.$$

(This equation is developed with the aid of the conception of the equilibrium box (van't Hoff) into which the reacting substances in dilute solution or the gaseous state are introduced through suitable semi-permeable membranes, in which the reaction proceeds, and from which the products are removed through suitable semi-permeable membranes, all isothermally and reversibly, the work done in the different steps being calculated by the aid of the gas laws.) The fraction of the second term of the right side of the equation is the equilibrium constant $K$. If the states of the substances are such that each exists independently before and after the reaction, then, even if $C_1^{n_1} = C_1'^{n_1'}$ as necessary for a catalytic change, the work done will be

the same whether the catalyst is present or absent, and the equilibrium will be unchanged. If, however, work is done in introducing or removing the catalyst, some sort of chemical compound is formed between two or more of the molecular species, whether this be termed chemical combination, solution, adsorption, physical change, etc., and then the terms involving the concentrations will not be the same as before. Thus the concentration term $C_1^{n1}$ may denote a complex containing the catalyst, while in the denominator the catalyst may be represented in a different complex. It may be said, therefore, that in the chemical changes as ordinarily observed, if a catalyst is involved in the reaction, that, as long as the substances are not present in the pure state or possessing the same properties before and after the reaction, there may well be a difference in the change in free energy of the reaction in the absence and presence of the catalyst and that the equilibrium will be changed correspondingly. That such changes have not been observed more frequently than has actually been the case is doubtless due to the small changes in the equilibria which have resulted by the addition of the catalyst. It must also be remembered that the law of mass action as developed in the thermodynamic treatment as indicated, holds only for dilute solutions and for gases at comparatively low pressures. For concentrated solutions and gases at high pressures, the theoretical considerations cannot as yet be applied satisfactorily.

## CHAPTER V.

### CHEMICAL REACTIONS; GENERAL CONSIDERATIONS.

In the preceding chapter chemical reactions were discussed with one condition fixed, namely, one substance involved in the reaction having the same chemical composition in the beginning and at the conclusion of the reaction. Such a reaction was treated as a catalytic reaction in which the substance unchanged in composition as a result of the reaction acts as the catalyst and causes a change in the velocity of the reaction. The explanation of such a change in velocity is to be found in the addition theory of chemical reactions according to which a reaction between two or more molecules takes place by the formation of a more complex intermediate compound which then breaks down again to form different molecules. The presence of the catalytic substance may accelerate the formation (or the decomposition) of the complex intermediate compound and in this way increase the velocity of the reaction, being itself reformed as one of the products of the decomposition of the intermediate compound. This theory of addition compound formation will now be applied to chemical reactions in general.

The formation of ammonium chloride was discussed to some extent in the preceding pages. The reaction is a common one, relatively simple, and as will be seen, representative of a large group of chemical transformations.

Omitting the influence of catalytic agents, this reaction may be considered to consist in the formation of the addition compound ammonium chloride from ammonia and hydrogen chloride. The simplest and most common way of express-

ing this reaction in the form of a chemical equation is the following:

$$NH_3 + HCl = NH_4Cl \qquad (1)$$

The reaction indicated by this equation does not take place under ordinary conditions with appreciable velocity. When ammonium chloride is obtained from ammonia and hydrogen chloride, water or moisture is present as a rule, and under these conditions, the reaction takes place rapidly. The equation as written does not, therefore, represent the reaction which is ordinarily observed. It is incomplete in that the possible action of the catalyst, water, is omitted. The action of the catalyst is of the highest importance here and any complete explanation of the reaction must necessarily include it.

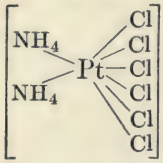
In the last chapter, it was pointed out that the action of the catalyst is due to the formation of addition compounds between the catalyst and the reacting components and that these addition compounds may then dissociate or undergo rearrangement, yielding the final reaction product and the catalyst.

In the particular reaction under discussion, the formation of ammonium chloride, water is known to form addition compounds with both the reacting components and with the final products. Before going into the details of this reaction, the reaction between ammonia, hydrogen chloride, and platinic chloride will be taken up, as it is analogous in certain respects, and will throw some light on the nature of the intermediate products or addition compounds.

The behavior of ammonia and hydrogen chloride toward platinic chloride is similar to their behavior toward water; that is, addition compounds are formed in both groups. Because of the different characters of the water and the platinic chloride, it is to be expected that the dissociation or decomposition of these addition compounds (in other

words, their stabilities, as measured by certain equilibrium constants) would not take place to the same extent. Bearing this difference in mind, the formulations may now be indicated.

The definite compound ammonium chlor-platinate, $(NH_4)_2PtCl_6$, is made up of, and may be prepared from, ammonia, hydrogen chloride, and platinic chloride. It may dissociate in a number of different ways, the most important of which are indicated by the following equilibria:



$$\begin{aligned} &= 2NH_4Cl + PtCl_4 && (a)\\ &= 2NH_3 + H_2PtCl_6 && (b)\\ &= 2HCl + (NH_3)_2PtCl_4 && (c)\\ &= 2NH_3 + 2HCl + PtCl_4 && (d) \end{aligned} \qquad (2)$$

The possible intermediary compounds such as $(NH_4)PtCl_5$ in equilibrium (*a*), $(NH_3)_2HPtCl_5$ in equilibrium (*c*), etc., are not given, as they add nothing to the principles which these equilibria are intended to illustrate. Equilibrium (*d*) represents the reaction between the three components and the "ternary" intermediate addition compound. The products formed according to the equilibria represented by equations (*a*), (*b*), and (*c*), may all be present, or only some of them may be formed. The extent to which the different products are found depends upon the equilibria of the various reactions under the conditions of temperature and pressure (or concentration) under which the reaction is being studied. The equilibria may, of course, be determined experimentally, and the values of the equilibrium constants give a measure of the relative chemical affinities of the reactions. If the conditions are such that, besides equilibrium (*d*), only or predominatingly the products shown by equilibrium (*a*) are present, then the platinic chloride plays the part of a catalyst in the formation of ammonium chloride from ammonia and hydrogen chloride. Again, if, besides equilibrium (*d*), mainly the products

given by equilibrium (*b*) are formed, then the platinic chloride is not the catalyst, but on the other hand, ammonia would be acting as the catalyst in the formation of hydrogen chlorplatinate from platinic chloride and hydrogen chloride. Similarly, if equilibrium (*c*) were the predominating reaction, hydrogen chloride would act as the catalyst in the formation of diammono platinic chloride from ammonia and platinic chloride. The concentrations of the reacting substances, according to the law of mass action, would control to a great extent in any given case, the nature of the products obtained. If the reaction is not allowed to go to completion, then the relative reaction velocities of the various reactions would determine the composition of the mixture at any instant.

This reaction is particularly instructive, since the composition of the intermediate addition compound is perfectly definite. With equilibria (*a*) and (*d*) it is seen that the platinic chloride acts as the catalyst for the reaction (either formation or decomposition, depending upon the concentrations of the reacting substances) between ammonia, hydrogen chloride, and ammonium chloride.

The influence of water on the reaction between ammonia and hydrogen chloride to form ammonium chloride may be taken up in the same way. Although very little is known of the way the water actually catalyzes the formation of ammonium chloride, the reaction considered in Chapter IV in the formation of tetraethylammonium iodide from triethyl amine and ethyl iodide in the presence of different solvents indicated the method of action of the catalyst. It was found that unsaturation of the solvent paralleled to a certain extent the increase in the velocity of the reaction. Ability to form addition compounds, intermediate or otherwise, seemed to be the controlling factor. Unfortunately, the composition of the intermediate addition compound is not so definite in the present case. In order

to show the reaction in as simple a form as possible, at the same time coinciding with the facts as far as known, it will be assumed that the "ternary" addition compound contains one molecule of hydrogen chloride, one molecule of ammonia, and one molecule of water. The formulation of the different equilibria, similar to equations (2), will then be as follows:

$$\left[\begin{matrix}\mathrm{HCl}\\ \mathrm{H_2O}\\ \mathrm{NH_3}\end{matrix}\right] \begin{matrix}= (\mathrm{H_2O.HCl}) + \mathrm{NH_3} & (a)\\ = (\mathrm{H_2O.NH_3}) + \mathrm{HCl} & (b)\\ = \mathrm{H_2O} + (\mathrm{NH_3.HCl}) & (c)\\ = \mathrm{H_2O} + \mathrm{NH_3} + \mathrm{HCl} & (d)\end{matrix} \qquad (3)$$

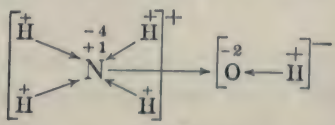
Starting with water, ammonia, and hydrogen chloride, [equilibrium (*d*)], it is found experimentally that ordinarily the products indicated by equilibrium (*c*) are obtained, or *vice versa*. Water acts as a catalyst for the reaction between ammonia, hydrogen chloride, and ammonium chloride, just as platinic chloride did in the preceding reactions. A difference between the two sets of reactions, (2) and (3), may lie in the fact that in the former, (2), the value of the equilibrium constants may be such as to show the intermediate "ternary" compound, ammonium chlorplatinate, to be more stable than the intermediate "ternary" compound in the latter, (3). Under different physical conditions, such as increase in temperature, etc., it is possible that the reaction in equations (3) would proceed in such a way as to favor the formation of the products of (*a*) or of (*b*). The changing of the values of the equilibrium constants when the conditions are varied may well cause the reaction to assume a different course. All the possibilities, with one molecule of each reactant, are given in the equations, however, and the deductions are similar to those from equations (2). The concentrations of the reacting substances here also play a predominating rôle in determining which products will be found in a reaction mixture.

The actual composition of the ternary compound is not known definitely, and has, therefore, been given in the simplest form, but even if different numbers of the reacting molecules were contained in it, the same principles and relations may be applied although the equations would be much more complicated. The relative velocities of the dissociation of the intermediate compound would determine which products are observed at any time, if the complete reaction has not been allowed to come to equilibrium. It is perhaps more usual to speak of the velocities of the various reactions than of the values of their equilibrium constants.

To return to the formation of ammonium chloride in the neutralization of ammonium hydroxide by hydrochloric acid, the equation for the change may be written as follows in which the presence of the solvent, water, is indicated:

$$HCl.H_2O + NH_3.H_2O = NH_3.HCl + 2H_2O.$$

It is evident that this reaction would amount to a change consisting in the replacement of water in the hydrate of hydrogen chloride by ammonia, or a replacement of water in ammonium hydroxide by hydrogen chloride. This reaction may be elaborated further. When an amine, such as ammonia, is dissolved in water, it combines, in part at any rate, with the water to form the addition compound written in its simplest form as $H_3N.OH_2$ (or graphically $\overset{+}{H}_3\overset{\overset{-3}{+1}}{N}\rightleftharpoons\overset{\overset{-3}{+1}}{O}H_2$ an onium addition compound). This compound may tautomerize to ammonium hydroxide, $NH_4OH$, the base from the ionic point of view, which may be written



in two zones to indicate the ionization, and which shows all

that is known structurally of the compound, except the formation of hydrates (which were indicated in a preceding chapter). When an acid, such as hydrochloric acid in water, reacts with this compound, in place of assuming a direct combination between hydrogen and hydroxyl ions as in the ionic theory, following the general schemes outlined, an addition compound is considered to be formed first. The complete reactions may be indicated in the most general way as follows:

$$(1)\quad NH_3 + H_2O = \begin{bmatrix} NH_3 \\ H_2O \end{bmatrix}, \quad (2)\quad HCl + H_2O = \begin{bmatrix} HCl \\ H_2O \end{bmatrix},$$

$$(3)\quad \begin{bmatrix} NH_3 \\ H_2O \end{bmatrix} + \begin{bmatrix} HCl \\ H_2O \end{bmatrix} = \begin{bmatrix} NH_3 \\ HCl \\ 2H_2O \end{bmatrix} = \begin{bmatrix} NH_3 \\ HCl \end{bmatrix} + 2H_2O. \quad (4)$$

In equations (1) and (2) one molecule of water is assumed to take part. The exact number is unknown and is immaterial for the principle. The "binary" compounds are written as double molecules. Tautomerism of these into the ionizable forms may take place and probably does so and reaction (3) to form the "ternary" compound follows the combination of the two "binary" compounds. This, then, may dissociate according to equation (4) to form ammonium chloride (or more probably a hydrate) and water. It must be recalled that these equations are all in fact really equilibria, and that the reverse reactions may also take place. Thus, if carbon dioxide, $CO_2$, were used in place of hydrogen chloride, very little of the products indicated in the equation corresponding to (4) would be present. This method of treating the subject includes also the generalizations derived from the ionic theory, such as, for example, the heats of neutralization of highly ionized acids and bases, which are practically identical in dilute solution. This is brought out by the following set of equations:

$$(1)\quad KOH + H_2O = \begin{bmatrix} KOH \\ H_2O \end{bmatrix} = \begin{bmatrix} K \\ H_2O \end{bmatrix}^+ + [OH]^-,$$

$$(2)\quad HCl + H_2O = \begin{bmatrix} HCl \\ H_2O \end{bmatrix} = \begin{bmatrix} H \\ H_2O \end{bmatrix}^+ + Cl^-,$$

$$(3)\quad \begin{bmatrix} KOH \\ H_2O \end{bmatrix} + \begin{bmatrix} HCl \\ H_2O \end{bmatrix} = \begin{bmatrix} KOH \\ HCl \\ 2H_2O \end{bmatrix} = \begin{bmatrix} KCl \\ 3H_2O \end{bmatrix} = \begin{bmatrix} K \\ 3H_2O \end{bmatrix}^+ + Cl^-$$

In dilute aqueous solution, in reactions (1) and (2) a greater number of molecules of water undoubtedly is involved than is indicated. The "ternary" addition compound of equation (3) is made up as indicated but may rearrange and then ionize. Comparing the final product of (3) with the substances present in great excess in (1) and (2), as shown by the determinations of the degrees of ionization, it is evident that the net change, since excess of water is present, is the combination of hydrated $H^+$ ion and $\bar{O}H$ ion, as postulated by the ionic theory. The mechanism of the change shows the part played by the solvent and brings the reaction into line with the general addition reactions of chemical changes.

To come back to the main subject, it becomes evident that many of the neutralizing, hydrolyzing, and double decomposition reactions are in fact nothing more than replacement reactions whose course is governed by the factors indicated, as well as by the atomic valences and coordination numbers of the constituents with respect to the particular substances which make up the intermediate addition compound.

Werner (l.c. pp. 232–7) has combined all these reactions into a general one, which may perhaps be indicated as follows:

$$\underset{(1)}{X_n[A_5MX]} + \underset{(2)}{H_2O} = \underset{(3)}{X_n[A_5MH_2O]X} = \underset{(4)}{X_n[A_5MOH]} + \underset{(5)}{HX}.$$

One molecule of water may react with compound (1) to

form compound (3). This primary compound may then dissociate to yield compounds (4) and (5). As a concrete example chromium chloride may be taken as the primary compound. Here M is Cr, X is Cl, and n is 2. The equation becomes:

$$\underset{(1)}{Cl_2[(H_2O)_5CrCl]} + \underset{(2)}{H_2O} = \underset{(3)}{Cl_2[(H_2O)_5Cr(H_2O)]Cl} = \underset{(4)}{Cl_2[(H_2O)_5CrOH]} + \underset{(5)}{HCl}.$$

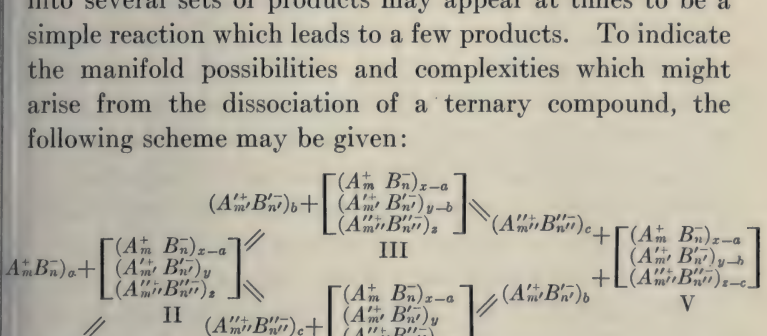
Compounds (1) and (2) combine to form (3); this is hydration. Compounds (1) and (2) undergoing double decomposition form (4) and (5); this is hydrolysis. The formation of (1) and (2) from (4) and (5) is neutralization. The formation of (1) and (2) or of (4) and (5) from (3) is dissociation.

In the same way that the formation of ammonium chloride from ammonium hydroxide and hydrochloric acid could be considered to be a displacement of water by hydrogen chloride, so it is possible to consider the above set of reactions in the case of the chromium chloride to be a set of displacement reactions. Compound (3) may be regarded as an addition compound containing both hydrogen chloride and water, since the part $\begin{bmatrix} HOH \\ CrCl \end{bmatrix}$ is equivalent to $\begin{bmatrix} HCl \\ CrOH \end{bmatrix}$. Compound (3) therefore can dissociate in either direction, giving as one of the products hydrogen chloride or water. The reaction in which compounds (1) and (2) form (4) and (5) (hydrolysis), is therefore a displacement of hydrogen chloride by water. Likewise, the reaction in which compounds (4) and (5) form (1) and (2) (neutralization), is a displacement of water by hydrogen chloride.

The reactions considered so far belong to the general

group which may be classed together and explained most satisfactorily as addition reactions, in which intermediate addition compounds are formed which are in equilibrium with various sets of products. If the initial and final products only are considered, then the reactions very often appear to be simple replacement reactions. In none of these reactions has the charge or state of oxidation of any of the atoms changed; that is to say, no oxidation or reduction has taken place. The treatment of the large and important group of reactions involving oxidation and reduction of different atoms in the molecules which take part in chemical reactions will be taken up in the chapters following these on addition and replacement reactions.

The dissociation of an intermediate addition compound into several sets of products may appear at times to be a simple reaction which leads to a few products. To indicate the manifold possibilities and complexities which might arise from the dissociation of a ternary compound, the following scheme may be given:



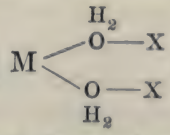

In this scheme, starting with $x$ molecules of $A^{+}_{m}B^{-}_{n}$, $y$ molecules $A'^{+}_{m'}B'^{-}_{n'}$, and $z$ molecules $A''^{+}_{m''}B''^{-}_{n''}$, the ternary addition compound I is formed. The molecules $A^{+}B^{-}$

are assumed not to exchange positive or negative constituents, but to dissociate as the integral molecules which make up the ternary compound. Under these simplified conditions, it is seen how the dissociation may take place, and the number of possible equilibria involved in a reaction of this type. If the various positive or negative constituents may in addition replace or displace each other, the number of equilibria is correspondingly increased. This scheme shows why the number of products in many organic reactions is so large. In inorganic reactions, in which the number of reacting components is smaller as a rule, the possibilities as to the number of products formed are smaller, but it must be emphasized again that the general principles of the mechanism of chemical reactions apply throughout, whether these be grouped for convenience of treatment or for any other reason as inorganic and organic reactions.

Since the ionic theory has been so successful in correlating a number of previously separated phenomena, including the possible explanation of certain chemical reactions, especially those taking place in aqueous solution, it is of importance to try to find to what degree the explanations based upon it are accepted at present, and how the objections may be met most satisfactorily by the newer developments. In this book the facts of the ionic theory are accepted, but some of the shortcomings of the theory, such as the part played by the solvent, have already been pointed out. It was shown how the mechanism of a number of chemical reactions might well be explained more satisfactorily on the basis of the addition theory. The statement made by a few zealous supporters of the ionic theory that only ions take part in chemical reactions may be dismissed without much consideration. This has never been the view of the greater number of workers who have always recognized the occurrence of reactions especially with organic compounds in which no ionization (as the

ionic theory understands ionization) was present. This fact, however, at once separates reactions into two groups, ionic and non-ionic. Just as with the suggestion of two kinds of valence, polar and non-polar, as shown in an earlier chapter, this divides chemistry into two branches, with separate sets of explanations for each. The addition theory includes all reactions and formulations, and offers one set of explanations for the two sets, at the same time including the relations developed by the ionic theory as part of the general development. Reference may be made to a paper by J. W. Walker (Trans. Chem. Soc. *85*, 1082 (1904)) in this connection. To indicate the application of the addition theory to inorganic reactions, a typical example of a reaction, explained heretofore on the basis of the ionic theory, will be described.

The reactions between some metallic salts, ammonium salts, and ammonia will be taken up briefly. Many of the bivalent metals such as nickel, magnesium, etc., form hydroxides insoluble in water but soluble in solutions of ammonium salts. The generally accepted explanation for the solubility in solutions of ammonium salts or for the non-precipitation by ammonia, if ammonium salts are present, is that the ammonium ion of the ammonium salts drives back or represses the electrolytic dissociation of the ammonium hydroxide so that the hydroxide ion is not present in sufficient concentration to exceed with the metal ion the solubility product of the metal hydroxide. The new explanation depends upon hydrolytic reactions and equilibria as outlined.

A bivalent metal halide, $MX_2$, will be chosen as an example. In water the compound  will be present and negative X combined with O carrying a pre-

dominatingly negative charge will ionize into $[M(OH_2)_2]^{++}$ and $2\bar{X}$. It is probable that a substance of this sort will take up more (generally four) molecules of water in onium combination with the metal element. These additional molecules of water are not directly involved in the theoretical views to be developed and will therefore be omitted. The substance $M(OH_2)_2X_2$ may undergo hydrolytic dissociation as shown in equilibrium (*b*) of the reaction.

$$M\begin{matrix}\diagup \\ \diagdown\end{matrix}\begin{matrix}H_2O\text{—}X \\ O\text{—}X\\ H_2\end{matrix} \rightleftharpoons [M(OH_2)_2]^{++} + 2\bar{X} \quad (a)$$

$$M(OH)_2 + 2HX \quad (b)$$

The reaction which will be observed depends upon the equilibria (affinity relationships) of (*a*) and (*b*) in the given equations, and upon the addition or removal of any of the products. For instance, equilibrium (*b*) will proceed to the right if a base is added. The addition of the base removes HX and causes more $M(OH_2)_2X_2$ to undergo hydrolysis until ultimately only $M(OH)_2$ will be present. This reaction will take place especially if $M(OH)_2$ is insoluble, but it is important to note from these equations that it is due to the removal of HX by the base rather than direct metathesis. The simplest way of looking at the change, if only the initial and final substances and their formulas are used, is $MX_2 + 2M'OH = M(OH)_2 + 2M'X$; but this, for one thing, leaves out of account the action of the solvent. Written in the ionic form $\overset{++}{M} + 2\bar{O}H = M(OH)_2$, while apparently going back to more fundamental relationships, does not show what direct part, if any, the solvent plays. By means of the equilibrium reactions as formulated, the part the solvent plays is made evident. Furthermore, the reaction is brought into line with a great number of others included among hydrolytic reactions.

Ammonia is analogous to water in its reactions. As stated before, onium compounds are formed to a greater or more readily observable extent with it than with water. If ammonia is added to a solution of $MX_2$, it is evident that a compound $(H_3N\rightleftarrows)_4M(\rightarrow NH_3\rightarrow)_2X_2$, or (omitting the four ammonias in onium combination with M), $M(NH_3)_2X_2$, may be formed. The relative amounts of $M(OH_2)_2X_2$ and of $M(NH_3)_2X_2$ which will be formed, or the distribution of $MX_2$ between water and ammonia, will depend upon the relative stabilities of these compounds under the given conditions. The substance $M(NH_3)_2X_2$ undergoes electrolytic dissociation as follows (omitting possible intermediate ions):

$$M\begin{matrix}H_3\\N\\N\\H_3\end{matrix}\begin{matrix}-X\\-X\end{matrix} = [M(NH_3)_2]^{++} + 2\overline{X}.$$

Ammonolytic dissociation to form $M(NH_2)_2$ and HX, analogous to the hydrolysis of the hydrated salt, does not seem to occur with these compounds under these conditions. (Possibly the mercury ammonia compounds dissociate in this way under suitable conditions.) The addition of a base has, therefore, no direct action on a substance of this formula in the way of influencing the equilibrium. Beyond the possibility of a direct metathetical reaction, the base plays no part, as it does in the hydrated salt, even if the hydroxide is not soluble. To sum up, the possible reaction between a base and a substance $MX_2$ in water in the presence of ammonium salts or ammonia, will depend upon the relative amounts of hydrated and ammoniated salt present; if an appreciable amount of the former is present, $M(OH)_2$ may be precipitated; if the salt is entirely present as the latter, no $M(OH)_2$ will be precipitated.

In the past years, F. Ephraim published some very careful studies on the stability of the metal ammoniates. He determined the temperatures at which the hexa-

ammonia (and substituted ammonia) derivatives of a number of salts of the bivalent metals (including Be, Ni, Co, Fe, Cu, Mn, Zn, Cd, Mg) showed definite vapor pressures. The results give a measure of the relative stabilities of these compounds, and consequently also for solutions of them. This gives no direct evidence as to the distribution of any given salt between water and ammonia with both present in solution, but does give a relative measure of the amounts of the ammoniates formed by a number of different salts. For instance, the salt $NiCl_2.6NH_3$ shows a vapor pressure of 500 mm. at 130°, while the salt $MgCl_2.6NH_3$ shows the same vapor pressure at 24.5°. This means that a very much smaller concentration of ammonia would be needed in solution to form the hexa-ammoniate with a nickel salt than would be necessary for a magnesium salt. Consequently, as a result of the distribution of the salt between the ammonia and the water, the concentration of ammonium salt needed to prevent the precipitation of the metal hydroxide if a base is added would be much less for the nickel salt than for the magnesium. The salts studied by Ephraim may be arranged in a series showing the relative amounts of ammonium salts needed to prevent precipitation if a base is added.

The views of Werner that compounds of the first order are not electrolytes but must go over into compounds of higher orders before becoming electrolytes bear upon this question. They have already been given and need only be mentioned here.

Reference may also be made to two experimental investigations bearing on this question: Isbekow [Z. anorg. Chem. *84*, 24 (1914)] found that by dissolving the substances mercuric bromide, antimony bromide, bismuth bromide, carbon tetrabromide, etc., in molten aluminium bromide as solvent, solutions were obtained which gave abnormally high molecular weights for the solute and which

conducted the electric current. Isbekow attributed this high molecular weight to association of the solute or to a combination of the solute with solvent, and thought that these complex substances were responsible for the ionization and conduction of the current. Isbekow's discussion of his results is of interest and may be given as follows:

"The associated condition of the electrolytes dissolved in $AlBr_3$ is not a general characteristic of molten salts and their mixtures. Although Lorenz [Z. phys. Chem. *70*, 230 (1910)] has shown that a marked association occurs in the case of molten salts, still as has been pointed out by the investigations of Sackur [Z. phys. Chem. *78*, 550 (1912)], the substances dissolved in molten salts, in many cases, break down into simple ions, and in dilute solutions of salts of the type $MX_2$ as solvent, the dissociation is complete. A relationship of this kind was also observed by Tolloczko [Z. phys. Chem. *30*, 705 (1899)] and by Klemensiewicz [Bull. de l'academie des Sc. de Cracowie (1908) p. 485)], in solutions of the alkali salts in $SbCl_3$. On the other hand, electrolytes dissolved in molten $HgCl_2$ show association as in $AlBr_3$. The individual influence of each solvent is also evident in the case of molten salts, one solvent possessing the ability to ionize principally simple molecules another principally complex molecules. Therefore, each electrolyte solution is undoubtedly the result of a particular interaction between the two components, since the same substance, in one solvent conducts and in the other does not. This interaction manifests itself in many cases in the participation of the solvent in the formation of the complex molecule or complex ion. It is not improbable, that in the above thermal experiments, such a participation of the solvent occurs." If Isbekow's interpretation is correct, the solvent and solute interact to form the electrolyte, similar to the formation of the ionogen ammonium chlorplatinate, $(NH_4)_2PtCl_6$, from platinic chloride and

ammonium chloride. The constitution of these ionogens would be of the form $(AlBr_3)_n(MX)_m$.

It was shown by Plotnikoff (J. Russ. Phys. Chem. Soc. (3) 466 (1902)) and later confirmed and studied more thoroughly by H. E. Patten (J. Physical Chem. *8*, 564 (1904)), that aluminium bromide dissolved in ethyl bromide gives a solution which has a relatively low electrical resistance, and from which aluminium may be deposited electrolytically just as in the case of a solution of an aluminium salt in water. Another interesting fact about these results is that ethyl bromide has a very low dielectric constant (8.9) and still serves as an ionizing medium for the aluminium bromide. This solution is analogous to the solutions described by Isbekow.

It must be borne in mind, however, in interpreting these last results, that the separation of a metal or other substance at an electrode bears no relation necessarily to the nature of the ions which may be present in solution. For example, copper may be deposited on the cathode from a solution of potassium copper cyanide, in which all except perhaps a minute part of the copper is contained in the anion.

Other evidence with regard to the combination of solvent and solute might be quoted, but the general trend of the views is apparent. As for the reasons for a substance being able to dissolve another substance and of inducing ionization, a number of suggestions have been put forward, especially for the latter phenomenon. Thus, W. Nernst and J. J. Thomson have considered it to be due to the dielectric constant of the solvent, J. Brühl to the (chemically) unsaturated nature of the solvent, etc. While all of these views possess a certain amount of truth for various solvents, there is at present no general explanation which covers all the facts. Possibly the development of the views put forward here involving addition compounds, tautomeric

rearrangements, and equilibria with different sets of products may permit of a more general theory, but at present, the quantitative data with regard to these addition products are too meagre to permit of more than a suggestion of this as a general explanation.

## CHAPTER VI.

### SOME CHEMICAL REACTIONS.

The principles developed in the preceding chapters will now be applied to chemical reactions, the substances reacting, and the probable mechanism or course of the reactions, involving at the same time a classification of these changes. The difficulty which arises in these applications is due to the wealth of material available, especially in the changes included in organic chemistry. There is a strong temptation to include all reactions which have been described and if this were done this book would resolve itself into a compendium of reactions, interesting perhaps in itself, but lacking a point of view by which it was intended to systematize such reactions as far as possible. The applications in this and the following chapter in the first place will include only reactions in which none of the atoms in any of the reacting molecules shall have changed its valence or become oxidized or reduced. Reactions involving such changes will be taken up in later chapters. In this and the following chapter a number of reactions will be discussed from the point of view of the mechanism or course of the reactions. Since so much material is available in the field of organic chemistry, practically all these reactions involve changes in organic compounds, and it will be shown how a number of reactions which heretofore have been considered to be different may be included in one general point of view. In the succeeding chapter, the changes which one group of substances, the olefins, undergo will be discussed and compared with the changes taking place in various organic and inorganic reactions. In this way, by considering first the changes involved in a series

of reactions, and then the changes undergone by a group of substances it is hoped to bring out the general principles involved in the mechanism of chemical reactions, without unduly elaborating the details of innumerable reactions.

The Friedel-Crafts reaction is one of the most useful reactions in preparative organic chemistry. In most text books, the reaction is discussed in connection with the synthesis of alkyl and acyl derivatives of the aromatic hydrocarbons. It will be seen in the following pages however that this is a somewhat misleading and incomplete view, since there are a great number of reactions involving the use of aluminium chloride which are not included in the above classification. With regard to the changes occurring in the Friedel-Crafts reaction, the aluminium chloride does not appear in the final product. The reaction as carried out in the laboratory is very often done in steps, first bringing together the components, perhaps in the presence of a diluent such as carbon disulfide; and second, decomposing the reaction mixture with water with the formation of the desired substance or substances and removal of the aluminium as chloride or hydroxide, etc. Since aluminium chloride may be present after the reaction has proceeded to a certain point, it may be assumed as a first consideration to play the part of a catalyst. A brief review of the theoretical explanations proposed at different times to account for the mechanism of the reaction will first be given.

C. Friedel and J. M. Crafts described the reaction in 1877 [J. pr. Chem. 16, 233.] Two typical reactions given by them were (1) the formation of amylbenzene from amyl chloride and benzene and (2) the formation of benzophenone from benzoyl chloride and benzene, both in the presence of aluminium chloride and giving hydrogen chloride as by-product. They suggested the following equations as an explanation of the first reaction:

$$C_6H_6 + Al_2Cl_6 = HCl + Al_2Cl_5C_6H_5,$$
(hypothetical compound)
$$Al_2Cl_5C_6H_5 + C_5H_{11}Cl = Al_2Cl_6 + C_6H_5(C_5H_{11}).$$

They assumed the formation of the hypothetical intermediate compound $Al_2Cl_5C_6H_5$ in this reaction and of similar compounds in other reactions. This theory has never been demonstrated experimentally to be true and has, therefore, been superseded by other theories.

The dominating idea in Friedel and Crafts' original theory and in most of the theories attempting to explain the reaction is the formation of more complex compounds first, followed by their decomposition or further reaction.

G. Perrier [C.r. *116*, 1300 (1893); Ber. *33*, 815 (1900)] found that in the Friedel-Crafts reaction for the formation of ketones from hydrocarbons and acyl halides, the acyl halides and also the ketones formed in the reaction formed addition compounds with the aluminium halides which he was able to isolate:

$$2RCOCl + Al_2Cl_6 = (RCOCl)_2Al_2Cl_6,$$
$$(RCOCl)_2Al_2Cl_6 + C_mH_n = 2HCl + (RCOC_mH_{n-1})_2Al_2Cl_6.$$

The decomposition of the addition compound (which formed a crystalline compound) with cold water yielded the ketone. The formation of these compounds has since been confirmed by several other investigators and has enabled them to study the kinetics of this reaction in the case of acyl halides.

G. Gustavson proposed the theory that the aluminium chloride formed intermediate addition compounds of the type $AlX_3C_6H_6$ and $AlX_3.3C_6H_6$ [J. pr. Chem. *68*, 209 (1903)], and that in the course of the reaction these addition compounds reacted with the alkyl halides to form the reaction products. For the preparation of these addition compounds, he passed dry hydrogen chloride into a mixture of aluminium chloride and the hydrocarbon [Ber. *11*, 2151

(1878)]. They could not be obtained in crystalline form however and recently some doubt has been cast on their existence. Gustavson finally succeeded in obtaining a crystalline compound which had the composition $2\ AlCl_3.2\ C_6H_3[CH(CH_3)_2]_3.HCl$ [C.r. *140*, 940 (1905); J. pr. Chem. *72*, 57 (1905)], but this does not conform to the above type and is really a ternary compound.

B. N. Menschutkin [J. Russ. Phys. Chem. Soc. *41*, 1089 (1909); Chem. Zentralb. *1910*, 1, 167] showed that the freezing point curves of mixtures of aluminium halides and benzene or toluene gave no indication of the formation of any such addition compounds as claimed by Gustavson. Many chemists are inclined to accept the results of Menschutkin as conclusive evidence that aluminium halides and benzene or toluene do not form any addition compounds. On the other hand, all that the freezing point curve shows under these conditions is that, even if formed, not enough of the addition compound was present to saturate the solution. Furthermore, Menschutkin found that in the case of other metal halides such as antimony chloride, addition compounds such as $SbCl_3.C_6H_6$ can be obtained [C. A. (1911) 1434)]. It must also be borne in mind in comparing these results with the results of Gustavson, that the latter in his experiments had hydrogen chloride present as well.

J. Böeseken and co-workers [Rec. trav. chim. *32*, 184 (1913); *33*, 317; *34*, 78; *35*, 109; Verslag Akad. Wenschappen *21*, 979] studied the Friedel-Crafts reaction in connection with sulfonyl chlorides such as p-brombenzenesulphonechloride, etc. These combined with the aluminium chloride. The resulting compounds then reacted with the aromatic hydrocarbon. The sulfone formed in the reaction combined with the aluminium chloride, and if formed in considerable amount decreased the velocity of the reaction by decreasing the concentration of the double salt of the sulfone chloride and aluminium chloride.

There is considerable experimental evidence at hand, therefore, for the formation of double salts or binary compounds from acid chlorides and aluminium halides. In addition to the examples given, E. P. Kohler [Am. Chem. J. *24*, 390 (1900)] iso'ated the compounds $AlBr_3.C_6H_5SO_2Cl$, $AlBr_3.C_6H_5COCl$, $AlBr_3.POCl_3$, $AlBr_3.C_6H_5COCH_3$, and $AlBr_3.C_6H_5NO_2$, and Abegg [Handbuch der anorganischen Chemie, vol. 3, part 1, p. 74 (1906)] mentions the compounds $AlCl_3.SCl_4$; $AlCl_3.2PCl_3$; $AlCl_3.2KCl$; $AlCl_3.4KCl$; $AlCl_3.4NH_4Cl$; etc. The ability of aluminium halides to combine to form complex compounds is also shown in the following substances which have been described:

$AlCl_3.HgCl.C_6H_6$ W. Gulewitsch [Ber. *37*, 1560 (1904)]; $AlCl_3.(C_2H_5)_2O$; $AlCl_3.C_6H_5OCH_3$; $AlCl_3.C_6H_5CO_2C_2H_5$; $C_2H_5Br.H_2S.AlBr_3$ [V. A. Plotnikoff, J. Chem. Soc. Abstr. (1913), 1, 1295], etc.

The evidence for the formation of binary compounds with aluminium halides and acyl halides, inorganic halides and a number of organic substances containing oxygen but no halogen is satisfactory. On the other hand, the evidence at hand concerning addition compounds from aromatic hydrocarbons and alkyl halides has failed to show their presence. For example, A. Wroczynski and P. A. Guye [J. chim. Phys. *8*, 189 (1910)] found that the freezing point curve of a mixture of benzene and chloroform gave only one eutectic, and Schmidlin and Lang observed the same with the benzene-bromoform system.

B. N. Menschutkin [Chem. Zentralbl. (1910), I, 167] and also J. Böeseken [Chem. Zentralbl. (1911), I, 466] suggested that in the Friedel-Crafts reaction the three reacting components combined to form a ternary compound which then reacted further. This view was adopted and elaborated by J. Schmidlin and R. Lang [Ber. *45*, 899 (1912)]. They considered the evidence for the existence of binary compounds described above, and concluded that the only satis-

factory explanation lay in the formation of ternary compounds. As positive evidence they cited the solubility of aluminium chloride in cold mixtures of benzene or toluene and alkyl halides forming filterable solutions which evolve hydrogen chloride upon being warmed, and also the increase in conductivity observed when benzene or toluene was added to a solution of aluminium chloride in ethyl bromide [J. W. Walker, Trans. Chem. Soc. *84*, 1082 (1904)].

There have been several other theories proposed for the mechanism of this reaction where no consideration was given to the existence of addition compounds. Among these may be mentioned the theory of J. U. Nef [Lieb. Ann. *298*, 253 (1897)]. He considers that the aluminium chloride splits out the hydrogen halide from the alkyl halide forming in this way an olefin which is added to the aromatic hydrocarbon. This is in line with his views concerning reactions of carbon compounds in general.

In conformity with the general principles outlined in previous chapters the view of the mechanism of the Friedel-Crafts reaction which will be adopted here will be that of Menschutkin, Böeseken, and Schmidlin and Lang, based upon the formation of a ternary compound. This view brings the Friedel-Crafts reaction in line with many other organic reactions, and permits of a more systematic classification of the various types.

In the Friedel-Crafts reaction then it may be assumed that a ternary compound consisting of aluminium chloride and the two reacting components is formed which is in equilibrium with various sets of substances. The following example will illustrate the formulations:

$$\left.\begin{matrix} C_2H_4 \\ C_6H_5H \\ HCl \\ AlCl_3 \end{matrix}\right\} = \left[\begin{matrix} C_2H_4 \\ HCl \end{matrix}\right] + C_6H_5H + AlCl_3, \qquad (a)$$

$$\left.\begin{matrix} C_2H_4 \\ C_6H_5H \\ HCl \\ AlCl_3 \end{matrix}\right\} = \left[\begin{matrix} C_2H_4HCl \\ AlCl_3 \end{matrix}\right] + C_6H_6, \qquad (b)$$

$$\left.\begin{matrix} C_2H_4 \\ C_6H_5H \\ HCl \\ AlCl_3 \end{matrix}\right\} = \left[\begin{matrix} HCl \\ AlCl_3 \end{matrix}\right] + C_6H_5C_2H_5. \qquad (c)$$

In this reaction, as generally viewed, ethyl benzene is formed from ethyl chloride, benzene and aluminium chloride. Some of the equilibria in this reaction with the ternary (or considering ethyl chloride to be made up of ethylene and hydrogen chloride, quarternary) intermediate compound are indicated. Only a few of the possible reactions are shown. Taking equilibria (*a*) and (*c*), it is evident that this represents the reaction as ordinarily viewed. In (*c*) of course the compound $\left[\begin{matrix}HCl\\AlCl_3\end{matrix}\right]$ may also be in equilibrium with its components. If acetyl chloride is used in place of ethyl chloride, a binary compound of acetophenone and aluminium chloride is formed which may be decomposed by water. The presence of aluminium chloride in the reaction mixture appears to favor the formation of condensation products, that is, more complex bodies from the simple substances. In the presence of aluminium chloride the products of certain definite equilibria are obtained. With other so-called "condensing agents" or catalysts, such as sulfuric acid or sodium hydroxide in place of aluminium chloride, other products may be formed due to other of the possible equilibria being favored. As indicated in Chapter V, a large number of equilibria and products are possible with a ternary compound. The part that a substance such as aluminium chloride plays in such reactions, is to cause certain definite equilibria to dominate over others as already indicated. Other added substances would cause other equilibria to dominate. For instance, if alkali were added to a mixture such as the above, the reaction by which ethylene and hydrogen chloride is formed from ethyl chloride might predominate. While there are definite differences in these changes, the principle which is brought out is that with a certain number of reacting substances which go to make up a ternary or even more complex compound and which is in equilibrium with a large number

of different sets of products, the addition of a new substance to the reacting mixture will cause certain of the reactions or equilibria to predominate over others, and each different added substance may result in a different equilibrium being observed experimentally. There is nothing said as to whether the added substance acts as a catalyst or not. This question is evidently a secondary one. From the theory of catalytic actions developed in Chapter IV, a reaction is catalytic if one of the reacting substances appears as an initial substance and final product. With acetyl chloride, benzene, and aluminium chloride, a compound of acetophenone and aluminium chloride is obtained. If the reaction is considered to be at an end here, aluminium chloride may be considered to act as a catalyst since its composition is unchanged. If, however, water is added to the reaction mixture, as is generally done experimentally, then the aluminium chloride is decomposed and would not be called a catalyst in the reaction. This view of the function of the action of aluminium chloride as a possible catalyst in the Friedel-Crafts reaction holds throughout. Whether it is assumed to act as a catalyst depends upon where the reaction is assumed to stop. In this connection it may be pointed out that the action of aluminium chloride has been considered by some from two points of view. Either it has been considered to act catalytically or as in an ordinary chemical action taking part in a definite stoichiometrical ratio; but it is seen that this difference is more one of definition and classification than a real difference in the mechanism of the reaction.

Since there is definite evidence in a number of the reactions that ternary or more complex intermediate compounds are formed, and there is evidence of complex compound formation with a number of other compounds of aluminium and similar metal halides, the general explanation of the Friedel-Crafts reaction may be taken to be that

indicated with a complex compound of the third or higher order as intermediate compound. The readiness with which such complex compounds are formed and their stabilities will depend evidently upon the nature of the reacting substances, and it should be possible to find regularities in the compositions of these reacting substances, upon which the ready formation of the condensation products in this reaction depends. A comparison of such groupings which facilitate this reaction (either by more rapid formation of intermediate products and their decomposition in certain directions, or in shifting the equilibria, or in some other way), with the groupings which facilitate the same or other condensation reactions in the presence of other catalytic or condensing agents, should be of value in developing the general theory of the mechanism of such reactions, of which the Friedel-Crafts reaction has been chosen as a well-known example.

A number of reactions which are aided or accelerated by aluminium chloride will now be given. Only the initial and the final products which are of immediate interest will be outlined. The probable complex intermediate compound will not be formulated although it will be understood to be present and involved in the different equilibria in every case. The reactions only in exceptional cases proceed quantitatively as indicated, and there are as a rule a number of other products formed in the reactions. These will not be indicated here. It is evident that a careful quantitative study of these reactions would be of great value.

1. $C_2H_5Cl + C_6H_6 = C_6H_5C_2H_5 + HCl.$
2. $CH_3COCl + C_6H_6 = CH_3COC_6H_5 + HCl.$
3. $CHCl_3 + 3C_6H_6 = CH(C_6H_5)_3 + 3HCl.$
4. $O_2NCCl_3 + 3C_6H_6 = O_2NC(C_6H_5)_3 + 3HCl.$
5. $C_6H_5CH_2CH_2COCl = \overline{C_6H_4 - CH_2 - CH_2 - CO} + HCl.$[1]

[1] F. S. Kipping, Trans. Chem. Soc. *65*, 480 (1894).

6. $CH_3COCl + CH_3COCl + CH_3COCl$
$= CH_3COCH_2COCH_2COCl + 2HCl$.[2]

7. $3C_3H_7COCl$
$= C_2H_5.CH.CO.CH(C_2H_5).CO.CH(C_2H_5).CO$[3]
$+ 3HCl$.

8. $(C_6H_5)_3CCl + HOCH_3$
$= (C_6H_5)_3COCH_3 + HCl$[4] (Etherification).

9. $CH_3Cl + C_6H_5NH_2.HCl$
$= C_6H_4(CH_3)N(CH_3)_2 + 3HCl$[4] (Alkylation of amines).

10. $C_2H_5Br + H_2S = C_2H_5SH + HBr$.[5]

11. $2C_6H_5CH_2Cl = (C_6H_5)_2C : C(C_6H_5)_2 + 2HCl$.[6]

12. $CH_2 : CH_2 + C_6H_6 = C_6H_5CH_2.CH_3$.[7]

13. $CH \vdots CH + C_6H_6 = C_6H_5CH : CH_2$.[8]

14. $CN.CN + C_6H_6 = CN.C(C_6H_5) : NH$.[6]

15. $CH_2.CH_2.CH_2 + C_6H_6 = C_6H_5.CH_2.CH_2.CH_3$.[9]

16. $C_6H_5.N : C : O + C_6H_6 = C_6H_5.NH.CO.C_6H_5$.[9]

17. $CO_2 + C_6H_6 = C_6H_5COOH$.[6]

18. $SO_2 + C_6H_6 = C_6H_5SO_2H$.[7]

19. $CO + C_6H_6 = C_6H_5CHO$.[10]

20. $O_2 + 2C_6H_6 = 2C_6H_5OH$.[7]

21. $S + C_6H_6 = C_6H_5SH$.[7]

22. $R.CH(CH_2)_2.CO.O + C_6H_6$
$= R.CH(OH)CH_2.CH_2.CO.C_6H_5$.[6]

23. $CHCl : CCl_2 + CCl_4 = CCl_3.CHCl.CCl_3$.[6]

24. $CHCl : CCl_2 + CHCl_3 = CHCl_2.CHCl.CCl_3$.[6]

[2] A. Combes, C. r. *103*, 814 (1886); Ann. chim. phys. [6] *12*, 199 (1887); F. S. Kipping, Proc. Chem. Soc. *9*, 208 (1893).

[3] A. Combes, C. r. *103*, 814 (1886).

[4] C. Friedel and J. M. Crafts, Ann. chim. [6] I, 503 (1884).

[5] V. A. Plotnikoff, J. Chem. Soc. Abstr. (1913) I, 1295.

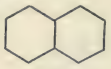
[6] H. J. Prins, J. pr. Chem. *89*, 14, 432 (for further references) (1914).

[7] C. Friedel and J. M. Crafts, Ann. chim. [6] *14*, 433 (1888).

[8] R. Varet and G. Vienne, Bull. Soc. chim. *47*, 918 (1887).

[9] S. Krapivin, Chem. Zentralb. (1910) I, 1335.

[10] L. Gatterman and J. A. Koch, Ber. *30*, 1622 (1897); Lieb. Ann. *347*, 347 (1906).

25. $C_2H_4 + HX = C_2H_5X$.
26. $C_2H_5ONO_2 + C_6H_6 = C_6H_5NO_2 + C_2H_5OH$.[11]
27. $C_5H_{11}ONO + C_6H_6 = C_6H_5NO + C_5H_{11}OH$.[11]
28. $ClCH_2CO_2C_2H_5 + C_6H_6 = C_6H_5C_2H_5 + ClCH_2COOH$.[4]
29. $ClCO_2C_2H_5 + C_6H_6 = C_6H_5C_2H_5 + HCl + CO_2$.[4]
30. $C_6H_5CH_3 + PCl_3 = C_6H_4(CH_3)PCl_2 + HCl$.[12]
31. $3CH_3I + CHCl_3 = CHI_3 + 3CH_3Cl$[13] ($CH_3Cl$ volatile).
32. $2C_6H_6 = C_6H_5.C_6H_5 + H_2$.
33. 2  $+H_2$ (4) (7)
34. $C_6H_6 + Br_2 =$ $C_6H_5Br + HBr$

The first striking fact in these reactions is the large number of different compounds whose reactions are accelerated by aluminium halides. Not all reactions which have been studied are included in this list, but the variety is sufficiently great to show the general applicability of the reaction. Those given may be divided into groups: Reactions 1 to 11 include the elimination of hydrogen halide in the formation of the condensation product; reactions 12 to 25 include direct addition of the components, accelerated by the presence of aluminium halide; reactions 26 and 27 show that nitrogen compounds may be included; reactions 28 and 29 that with certain groupings, in place of the elimination of hydrogen halide as the dominant reaction, different groups may be eliminated; reaction 30 shows a further possibility; while reactions 31 to 33 are in reality oxidation-reduction reactions and should be treated in a later chapter but are included here for the sake of completeness; and reaction 34, really an oxidation-reduction reaction also, is included to show the action of halogenation. A number of other reactions which are catalyzed by aluminium

[11] E. Boedtker, Bull. Soc. chim. IV (3) 726 (1908).
[12] A. Michaelis and C. Panek, Ber. *13*, 653 (1880).
[13] J. W. Walker, J. Chem. Soc. *85*, 1089 (1904).

chloride but which are in reality oxidation-reduction reactions in the sense that certain atoms in the molecules change their valence or state of oxidation, may be mentioned. For example, xylene at its boiling temperature with the addition of 2 to 4 per cent. aluminium chloride yields 12 per cent. toluene and also benzene and polymethylated benzene (F. Fischer and H. Niggeman, Ber. *49*, 1475 (1916). The action of aluminium chloride on petroleum was studied by A. Pictet and I. Lercynska (Bull. soc. chim. IV, *19*, 326 (1916)). Cyclohexane was found to rearrange in part to methylpentamethylene on heating to boiling for 48 hours in the presence of aluminium chloride (I. Aschan, Lieb. Ann. *324*, 1 (1902)).

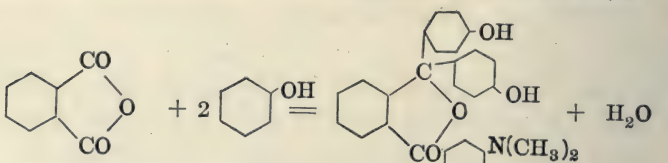
In addition to the evidence regarding complex addition compounds already given, another line of proof may be mentioned. The reacting mixtures in the Friedel-Crafts reaction as a rule develop more or less color, starting with colorless compounds. The formation of colored compounds in the case of somewhat different reactions has been taken to show addition compounds [J. Kendall, Jour. Amer. Chem. Soc. *37*, 149 (1915) for aldehyde and ketone addition compounds with acids, and H. Wieland and E. Wecker, Ber. *43*, 699 (1910) as forerunners of a number of substitution reactions.]

With regard to the chemical constitutions or structures of the intermediate addition compounds, not much can be said. The element which appears to be specifically responsible for the formation of these compounds is aluminium. Aluminium salts readily form "onium" or molecular compounds or compounds of the second and higher orders. The occurrence of complex aluminium salts in nature, such as the aluminium silicates, bauxite, etc., shows that complex inorganic aluminium compounds are capable of existing and are apparently extremely stable. The complex organic compounds of aluminium, some of which have been proven

to exist and others which are assumed to be formed in the Friedel-Crafts reaction, parallel these inorganic compounds. The difference between the two sets lies in the tendency of the organic part of the compounds to reach a more stable condition and the velocity with which this condition is attained. Otherwise the two sets of compounds are similar. Besides the fact that chemical combination is probably due primarily to the ability of the aluminium to form onium compounds under the given conditions, it is difficult to say more at present with regard to the chemical structures of these complex intermediate compounds.

In place of the aluminium chloride used in the Friedel-Crafts reaction, it has been found that some of the chemical changes may be accelerated by the addition of other catalysts to the reaction mixtures. Anhydrous zinc chloride has been used to some extent in this way. The following reactions are a partial list of such changes. The part played by the zinc chloride, in the formation of the probable complex intermediate compounds and the equilibria of the latter with various sets of products, is omitted and only the main reactions or changes are shown just as in the Friedel-Crafts reaction.

35. $2CH_3OC_5H_{11} + C_6H_5COCl \rightleftharpoons \begin{matrix} CH_3Cl + CH_3CO_2C_5H_{11} \\ C_5H_{11}Cl + CH_3COOCH_3 \end{matrix}$.

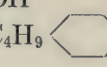
36. 

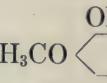
37. $C_6H_5CCl_3 + 2\,C_6H_5N(CH_3)_2 = C_6H_5CCl(C_6H_4N(CH_3)_2)_2 + 2\,HCl$

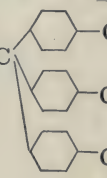
38. $Cl_3CHO + 5C_6H_5N(C_2H_5)_2 = [(C_2H_5)_2NC_6H_4]_3C.CH[C_6H_4N(C_2H_5)_2]_2 + H_2O + 3HCl.$

39. $C_6H_5CHO + CH_3NO_2 = C_6H_5CH:CHNO_2 + H_2O.$

40. $(CH_3)_2(C_2H_5)C(OH) + C_6H_5OH$

$= C_4H_9$  $- OH + H_2O.$

41. $CH_3COOH +$ $= CH_3CO$  $-OH + H_2O.$

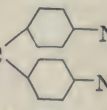
42. $HCOOH + 3C_6H_5OH = HC$  $+ 2H_2O.$

It is evident that zinc chloride is almost as universal a catalyst for such reactions as aluminium chloride, and undoubtedly it would be found experimentally that in many of the Friedel-Crafts reactions zinc chloride would answer as well as aluminium chloride.

Concentrated sulfuric acid is also employed very often in such condensation reactions. It can be used in reaction 36 as well as zinc chloride. Other reactions in which it has been used as catalyst are as follows (formulated in the same way as the preceding reactions):

43. $2C_6H_6 + (CH_3O)_2CH_2 = (C_6H_5)_2CH_2 + 2CH_3OH.$

44. $2C_{10}H_8 + CH_2O = H_2C(C_{10}H_7)_2 + H_2O.$

45. $2C_6H_5NO_2 + CH_2O = H_2C$  $+ H_2O$

46. $C_6H_5CHO + 2C_6H_6 = CH(C_6H_5)_3 + H_2O.$

47. $C_6H_4$ $CHO + CH_3COCH_2Cl$

$= C_6H_4$ $CH : CH.COCH_2Cl + H_2O.$

Other catalysts or so-called condensation agents may be considered in the same way. Without elaborating further, it may be said that the same principles apply to all these reactions; the formation of a complex intermediate addition

product which may be in equilibrium with various sets of products, and the course of the reaction in the presence of a definite catalyst being dependent upon the concentrations of the various reacting substances according to the principle of mass action and the relative velocities of the reactions if equilibrium has not been attained. In a number of cases the intermediate compound has been isolated. The reactions are quantitative only in exceptional cases. As a rule a number of products are obtained, but those given in the above equations represent the products which were of interest at the time the reaction was studied.

It will have been observed that a certain awkwardness in nomenclature has occurred in the discussion of the reactions. In the formulations of the different reactions, equilibria have been spoken of at times without the intention of conveying the meaning that the various substances taking part existed at definite equilibrium concentrations. The term equilibrium was used in these cases in place of the more usual "chemical equation" to emphasize the significance of reversibility and mass action effect.

A definite group of reactions which has been studied extensively is that in which a nitro-group is introduced into an organic compound, combined with carbon and in place of a hydrogen atom. This reaction is commonly known as nitration, but in conformity with the general chemical nomenclature it should be called nitronation. However, for the present in this book, the older term nitration will be used. Before taking up nitration reactions in detail, some general relations developed in the reactions already considered and some additional ones will be discussed briefly.

It is well known that the presence of certain side chains on the benzene nucleus facilitates the introduction of various substituent groups in place of the hydrogen of the benzene nucleus. This is true for the Friedel-Crafts re-

action, halogenation, sulfonation, nitration, etc. The question of the possible relation of this phenomenon to the mechanism of the reactions has been studied more carefully in nitration than in other reactions.

It has been found that aniline, phenol, and similar compounds of this type are nitrated to a greater extent by a given strength of nitric acid than is benzene itself. It has been observed quite frequently that an intermediate compound is formed in which a hydrogen of the amino or hydroxyl group on the benzene ring has been replaced by the nitro or other entering group. This compound then rearranges under certain conditions so that the entering group substitutes in the ortho or para position. Such rearrangements are very general and were first studied systematically for the rearrangement of hydrazobenzene to benzidine. This type is therefore commonly known as the benzidine rearrangement. The question has been considered whether such intermediate compounds always occur in the nitration, etc., of derivatives of benzene when ortho and para derivatives are obtained, or whether substitution in the ortho and para positions can take place directly. This led to the development of two theories of substitution: (1) Direct substitution, which takes place with benzene compounds having an amino or hydroxyl group already present; (2) Indirect substitution, which always occurs when ortho and para compounds are formed. Holleman carried out a serie of experiments to test these views, and came to the conclusion that it is not essential for an intermediate compound such as is assumed in indirect substitution to be formed, and that indirect and direct substitution are essentially the same.

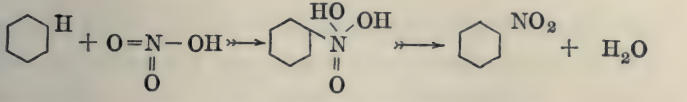
In discussing this question, it seems simplest to look upon it as analogous to the etherification of alcohol with sulfuric acid as catalyst. In this reaction, it has been suggested that the etherification takes place in several

steps; first the formation of ethyl hydrogen sulfate, and then the action of more alcohol with the latter to form ether. The evidence adduced by those holding this view is that ether can be formed by starting with ethyl hydrogen sulfate and that ethyl hydrogen sulfate can be formed from ethyl alcohol and sulfuric acid, and therefore that the ethyl hydrogen sulfate is an intermediate product which is always formed. It has been pointed out in a previous chapter however that a more correct view of this reaction is that the ethyl alcohol and sulfuric acid form an addition compound which can dissociate in different ways and is therefore in equilibrium with various sets of products; for example, to form ethyl hydrogen sulfate in one reaction; ether in another, olefin in another, and so on. The product actually obtained depends upon the conditions (chemical and physical) as already pointed out.

It seems that the question of indirect substitution is a similar one and that here also an intermediate addition compound is formed which may dissociate on the one hand to form a compound with the substituent in the side chain, and on the other hand with the substituent in the benzene nucleus.

In taking up a more detailed study of nitration, the general methods of preparing nitro compounds may first be mentioned. The usual methods involve the action of nitric acid alone, or in the presence of sulfuric acid, or of water, or of a non-ionizing medium such as ether. Other methods involve the use of ethyl nitrate or of nitrosulfates ($NO_2.OSO_2.OH$), nitroacetates (or acetyl nitrate), etc. For methods used in isolated cases reference must be made to the books of Weyl, Lassar-Cohn, and others.

J. U. Nef's view of nitration is of interest. He considers the reaction to be analogous to an aldol condensation and formulates it as follows (Jour. Amer. Chem. Soc. *26*, 1566 (1904)):



His general theory for this and similar reactions may be given in his own words: "Excluding reactions called ionic, a chemical reaction between two substances always first takes place by their union to form an addition product. The one molecule being unsaturated and in a partially active condition absorbs the second molecule because it partially splits or dissociates it into active portions. The resulting addition product then often dissociates spontaneously, giving two new molecules. The similarity of such reactions to those called ionic is at once apparent, but their relationship cannot, in the present state of our knowledge, be clearly understood." Nef's view of this reaction is similar to the one developed here and differs mainly in that he formulates the manner in which the hydrogen atom of the benzene acts specifically.

Nitro compounds may be obtained by the action of ethyl nitrate and aluminium chloride. Since many of the Friedel-Crafts reactions may be carried out with sulfuric acid in place of aluminium chloride, and since in nitration with nitric acid, sulfuric acid is very often used, the fact is brought out again that nitration belongs to the same general type of reaction as the Friedel-Crafts reaction. This similarity may be brought out in the following manner. The reaction

$$\underset{(A)}{2C_6H_5} + O = \underset{(B)}{C{<}^{R}_{R}} \rightarrow C_6H_5{-}C{<}^{C_6H_5}_{R} + H_2O$$

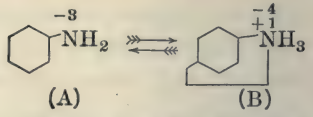
is accelerated either by sulfuric acid or aluminium chloride In the compound (*B*) the oxygen atom plays the part of the chlorine in the usual Friedel-Crafts reaction. If in place of the oxygen compound, the ketone, *B*, the oxygen compound nitric acid be substituted, the reaction would be similar. The same is true if (*B*) represented an aldehyde.

Such reactions with aldehydes were illustrated in reactions 44 to 47 above where sulfuric acid was the special catalyst. Reaction 26 illustrated nitration with ethyl nitrate and aluminium chloride. Remembering the fact that in the final product condensation has taken place with the elimination of the oxygen of the ketone, aldehyde, or nitric acid, whether the catalyst was sulfuric acid or aluminium chloride, and comparing the initial and final products obtained with the initial and final product of the reaction when a base is neutralized by an acid;

$$HX + BOH = BX + H_2O$$

it is evident that the benzene plays the part of the acid, and the ketone, aldehyde, or nitric acid that of the base.

In discussing the entrance of a new substituent in a benzene derivative, it will be found that a number of reactions can be very much simplified if it is considered that the para (or ortho) hydrogen atom to the group present takes part in the reaction. To explain by means of an example: In aniline it may be assumed that an equilibrium exists between the two tautomeric forms

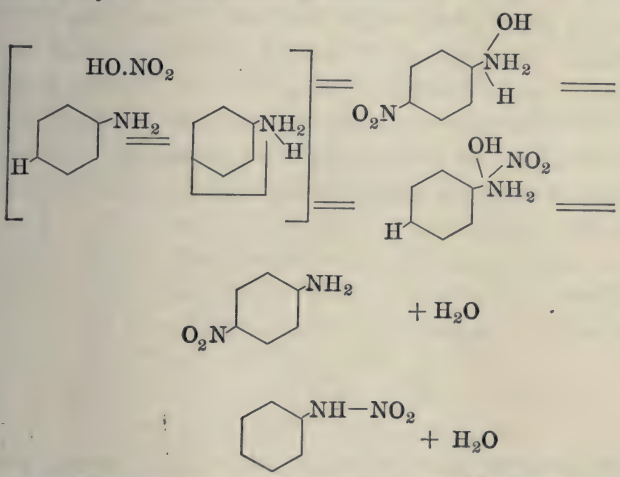



(A) (B)

In (*B*) the nitrogen is in the onium form, and the benzene nucleus (or more strictly, the para carbon atom) plays the part of the acid. This equilibrium is similar to the one present in glycine; namely, $HO_2C.CH_2.\overset{-3}{N}H_2 \rightleftharpoons O.OC.CH_2.\overset{-4}{\underset{+1}{N}}H_3$

There is evidence to show that the equilibrium exists in the latter case. In the former, the assumption of such a similar equilibrium helps to explain a number of reactions, in fact, it may be taken to be the fundamental phenomenon in all "benzidine rearrangements."

Taking the simplest case, the nitration of benzene, the reaction may be formulated as follows:




These equilibria represent a more or less ideal case, since as a rule other substances are present, and also the nitroamine which may be formed reacts farther. If sulfuric acid is present, a ternary intermediate compound would be formed. If acetanilide were used instead of aniline, the general reaction would be similar. If, however, a large excess of sulfuric acid were used in the reaction, then the aniline would be present practically entirely as aniline sulfate and there would not be the tautomeric form present. Under these circumstances, the intermediate compound would not be the same as before, and the nitration would proceed as if benzene itself were being nitrated. Mainly meta compound would be obtained under these conditions. The velocity of nitration of benzene derivatives containing different substituents was studied by H. Martinsen [Z. physik. Chem. *50*, 385 (1905); *59*, 605 (1907)]. He found the velocities to be dependent upon the substituents in the following way:

$$NO_2 < SO_3H < CO_2H < Cl < CH_3 < OCH_3 < OC_2H_5 < OH.$$

Smaller velocity ← → greater velocity

Those groups which when present diminish the velocity orient the nitro group into the meta position, those which increase the velocity orient the nitro group into the para and ortho positions. A reason for the increase in the velocity of substitution by amino and hydroxyl groups may well be due to the unsaturation of these groups and their ability to form addition compounds. The nitro, sulfonic acid, etc., groups being more saturated, have the opposite effect.

In the nitration in the presence of sulfuric acid, W. Markownikoff [Ber. *32*, 144 (1899)] and others consider the nitrating agent to be nitrosulfuric acid,

In the presence of acetic anhydride or acetic acid, a similar compound of nitric and acetic acids, acetyl nitrate, is assumed [A. Pictet and P. Genequand, Ber. *35*, 2526 (1902)], and with benzoic acid, benzoyl nitrate [R. Willstätter, Ber. *42*, 4152 (1909)]. Whether these compounds play the part assigned is similar to the question of whether ethyl sulfuric acid is always formed in the preparation of ether, and may be handled similarly. If it is formed at some stage of the reaction, it will probably be more able to form an addition compound, since it is obtained by loss of the elements of water from two other molecules and is probably more unsaturated. In this way, the velocity of the reaction might be accelerated, but an intermediate addition compound would still be formed.

Nitration in solvents other than water is to be preferred at times. In acetic acid for example, besides the advantages just spoken of, the solvent effect of the acetic acid may be of aid in increasing the concentration of the hydrocarbon. Such conditions as the hydrogen ion concentration of the mixture may also play a part and may be influenced favor-

ably by changing the solvent. Another factor to be considered is that in some reactions nitric acid will cause oxidation, and the choice of the solvent will sometimes obviate this. These special cases have not as yet been investigated quantitatively with sufficient care to enable general conclusions to be drawn as to the reasons for these conditions.

Aliphatic nitro compounds cannot as a rule be prepared in the same way as the aromatic nitro compounds. The more rapid oxidation of aliphatic hydrocarbons by nitric acid is the main interfering factor, so that conditions must be chosen which minimize oxidation and promote nitration. The oxidation reactions are of such complexity in these cases that no attempt will be made to formulate them. Only a summary of the conditions favoring nitration will be given. The use of a solvent such as ether for carrying out the reaction is often successful. Also dilute nitric acid has been used, and alkyl (generally ethyl) nitrate. In the Friedel-Crafts reaction with ethyl nitrate, aluminium chloride is used as catalyst. In aliphatic nitrations with ethyl nitrate, alkalis such as metal alkoxides ($NaOC_2H_5$) are found to be best. The use of alkalis brings out the similarity of this reaction to aldol condensations which are also favored by alkalis. An example of aliphatic nitration, in comparison with an aromatic one may be given:

$$C_2H_5ONO_2+H_2C\begin{matrix}COCH_3\\CO_2C_2H_5\end{matrix}\xrightarrow{NaOC_2H_5}NO_2CH\begin{matrix}COCH_3\\CO_2C_2H_5\end{matrix}+C_2H_5OH,$$

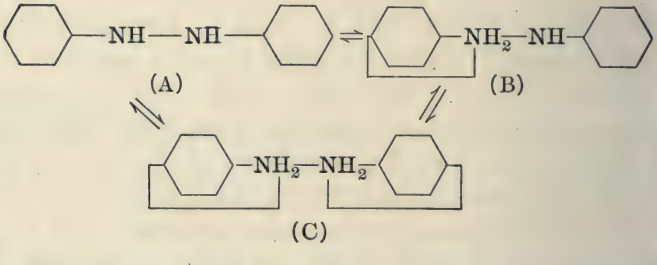
$$C_2H_5ONO_2+H.C_6H_5\xrightarrow{AlCl_3}NO_2C_6H_5+C_2H_5OH.$$

The presence of unsaturated or so-called "negative" groups on the carbon atom being nitrated appears to be necessary for a satisfactory carrying out of the reaction.

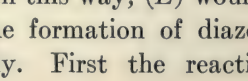
Another method for the aliphatic nitration is the reaction of alkyl halide with silver nitrite, in which considerable nitro compound is formed. With alkali nitrite on the other hand, very little nitro compound is formed. This difference

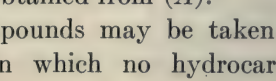
is evidently due to the different oxidizing potentials of the silver and the alkali, and the equilibria between various sets of products and the intermediate addition compound. Similar questions come up with other sets of isomeric compounds, cyanides and isocyanides; oxygen and nitrogen ethers of cyanic acid, etc. This question will be taken up again in a later chapter.

While the explanation of the benzidine rearrangement has been applied specifically to nitration only, it evidently holds for all similar reactions. With benzidine, the formulation may be given as follows:




Equilibrium may exist between the three compounds (*A*), (*B*), and (*C*). In the presence of strong acid or other suitable catalytic agent, complex additions of (*A*), (*B*), and (*C*) with the former may take place, and these may then decompose in different directions, giving in addition to (*A*), (*B*), and (*C*), compounds such as




etc. The conditions of the reaction, such as the formation of more stable salts from the sulfuric acid and (*D*) or (*E*) may control the yield of the different products obtained, and in this way, (*E*) would be obtained from (*A*).

The formation of diazo compounds may be taken up briefly. First the reactions in which no hydrocarbon

radicals are present will be described. It will be recalled that in the formation of amides the reaction was treated in the same way as the formation of esters from acids and alcohols;

$$AOH + HNH_2 = ANH_2 + H_2O,$$

or

$$\begin{bmatrix} A\ H \\ \\ H_2O \end{bmatrix} + NH_3 = \begin{bmatrix} A\ H \\ H_2O \\ NH_3 \end{bmatrix} = \begin{bmatrix} AH \\ NH_3 \end{bmatrix} + H_2O.$$

The same principle can be used to explain the formation of amides of nitric and nitrous acids (or the formation of nitroamines and diazotization). If $A = NO_2$, then

$$O_2NOH + NH_3 = O_2NONH_4 = \underset{\text{or}}{\begin{bmatrix} O_2NOH \\ NH_3 \end{bmatrix}} \quad \underset{\text{or}}{O_2NNH_2 \quad [N_2O + H_2O]} + H_2O,$$

and if $A = NO$

$$ONOH + NH_3 = ONONH_4 = \underset{[N_2 + H_2O]}{ONNH_2} + H_2O.$$

The nitroamine and nitrosoamine are unstable under ordinary conditions (since nitrogen apparently does not possess the inertia of carbon), differing in this way from the nitro-derivatives of the hydrocarbons. Nitroamine, known often as nitramide, or its tautomer, hyponitrous acid, decomposes readily into nitrous oxide and water, while nitrosoamine forms nitrogen and water (analogous to diazo compounds).

It was pointed out in the Friedel-Crafts reaction that the hydroxyl group or a chlorine atom might be eliminated in the condensations; for example,

$$ROH + HC_6H_5 \rightarrow RC_6H_5 + H_2O,$$

or

$$RCl + HC_6H_5 \rightarrow RC_6H_5 + HCl.$$

Similarly with the reactions with ammonia,

$$AOH + HNH_2 \rightarrow ANH_2 + H_2O,$$

or

$$ACl + HNH_2 \rightleftharpoons ANH_2 + HCl.$$

The action of nitrosyl chloride on ammonia is similar; namely,

$$ONOH + HNH_2 \rightleftharpoons ONNH_2 + H_2O,$$

and

$$ONCl + HNH_2 \rightleftharpoons ONNH_2 + HCl.$$

The action of nitrous acid on amines is indicated very often as follows:

$$RNH_2 + ONOH \rightleftharpoons RN_2OH + H_2O.$$

In looking at this reaction from the point of view of intermediate addition compound formation, it is evident that it belongs to the same group of reactions. The intermediate addition compound might be formulated $\begin{bmatrix} \text{olef. } HNH_2 \\ ONOH \end{bmatrix}$ and the following components can be recognized and would be present in the various equilibria,

$$H_2O, \text{ olef.HOH}, RNH_2, HNO_2, NH_3, \text{ etc.}$$

The diazotization reaction may also be formulated similarly to the action of a base on an acid:

$$BOH + HA = BA + H_2O,$$
$$ONOH + HNHR = ONNHR + H_2O.$$

With nitrosyl chloride or ethyl nitrite in place of nitrous acid, the same holds except for Cl or $OC_2H_5$ instead of OH. The nitrous acid in this reaction corresponds to the base, and the amine to the acid. This formulation also shows how general a classification may be developed from a simple scheme and that although the reactions of organic chemistry appear to be most complex and different, in reality a great many conform to simple fundamental principles and changes. If $A = C_6H_5$, then the reaction corresponds to the formation of nitrosobenzene, etc.

It has been noticed that in some reactions the part played by alcohols corresponds to the part played by the acid, HA; for instance, in the formation of esters from acid chlorides and alcohols, in the type reaction

$$BX + HA = BA + HX.$$

This corresponds to the neutralization reaction just given except that X is used in place of the OH. The general principle of intermediate compound formation, though not mentioned every time, must be understood to apply to all these reactions. If nitrous acid plays the part of BX and an alcohol that of HA, then the ready formation of nitrite esters is not surprising when the two interact. From this point of view the nitrite esters are the aquo-esters of nitrous acid, and diazo compounds are the ammono-esters of nitrous acid, ON.OR and ON.NHR (not considering tautomeric rearrangements within the molecule).

## CHAPTER VII.

### SOME CHEMICAL REACTIONS (CONTINUED).

THE discussion of the mechanism of the reactions considered so far may be summarized as follows:

(1) Reactions occurring in organic chemistry are similar to those in inorganic chemistry.

(2) The theory of reactions in aqueous solutions, heretofore based upon ionization relationships, can be accounted for by addition compound formation involving the solvent.

(3) All reactions appear to take place through the intermediate formation of an addition compound. If the reaction is catalytic, the catalyst is one of the components of the addition compound.

(4) When water is considered as the catalyst for reactions taking place in aqueous solutions, the hydrates formed may give rise to ionization.

The reactions may be based upon the general equation:

$$BX + HA = BA + HX.$$

They may be grouped in outline as follows:

I. Neutralization of an acid by a base; $B$ = metal, $X$ = OH, $A$ = acid group.

$$NH_4OH + HCl = NH_4Cl + H_2O,$$
$$NaOH + HCl = NaCl + H_2O.$$

Water may act as the catalyst in these reactions.

II. Friedel-Crafts reaction; B = R, X = Cl or OH, A = $C_6H_5$, etc.

$$RCl + HPh = RPh + HCl,$$
$$ROH + HPh = RPh + H_2O.$$

Aluminium chloride, zinc chloride, sulfuric acid, hydrogen chloride, etc., may act as the catalyst.

III. Aldol condensation; BX = aldehyde or ketone, A = so-called "negative" group combined with $\alpha$-carbon atom.

$$\begin{matrix} RC = O \\ H \end{matrix} + H_2CA_2 = RCH : CA_2 + H_2O.$$

Various catalysts; zinc chloride, hydrogen chloride, alkalies, etc.

IV. Esterification; B = alkyl, A = acid group, X = Cl or OH.

$$ROH + HA = RA + H_2O,$$
$$RCl + HA = RA + HCl.$$

Catalysts; zinc chloride, sulfuric acid, hydrogen chloride, etc.

V. Etherification; B = alkyl, A = alkoxyl group, X = Cl or OH.

$$ROH + HOR' = ROR' + H_2O,$$
$$RCl + HOR' = ROR' + HCl.$$

Catalysts as in reactions IV.

VI. Amide formation; B = acyl group, X = OH or Cl, A = amino group.

$$AcOH + HNH_2 = AcNH_2 + H_2O,$$
$$AcCl + HNH_2 = AcNH_2 + HCl,$$
$$AcOH + HNR_2 = AcNR_2 + H_2O.$$

VII. Amine formation; B = alkyl or aryl group, X = Cl or OH, A = amino group.

$$ROH + HNH_2 = RNH_2 + H_2O,$$
$$RCl + HNH_2 = RNH_2 + HCl,$$
$$ROH + HNR_2' = RNR_2' + H_2O.$$

VIII. Formation of nitro compounds; B = $NO_2$, X = OH or substituted OH group, A = alkyl or aryl group.

$$O_2NOH + HC_6H_5 = O_2NC_6H_5 + H_2O,$$
$$O_2NOC_2H_5 + HC_6H_5 = O_2NC_6H_5 + C_2H_5OH,$$
$$O_2NOSO_2OH + HC_6H_5 = O_2NC_6H_5 + H_2SO_4,$$
$$O_2NO_2CCH_3 + HC_6H_5 = O_2NC_6H_5 + HO_2CCH_3.$$

IX. Formation of nitroso compounds; B = NO, X = OH, Cl, or substituted OH group, X = alkyl or aryl group.

$$ONOH + HC_6H_5 = ONC_6H_5 + H_2O,$$
$$ONCl + HC_6H_5 = ONC_6H_5 + HCl,$$
$$ONOC_2H_5 + HC_6H_5 = ONC_6H_5 + C_2H_5OH.$$

X. Diazotization; B = NO, X = OH or Cl, A = amino or alkylated or arylated group.

$$ONOH + HNHR = ON_2HR + H_2O,$$
$$ONCl + HNHR = ON_2RH + HCl.$$

XI. Benzidine rearrangement; B = $NO_2$, X and A = $NHC_6H_4$.

$$O_2N - \overbrace{\underbrace{NH - C_6H_4}H} = \overset{H}{\underset{|}{N}}H - C_6H_4 - NO_2.$$

Catalysts: sulfuric acid, phosphorus pentachloride, etc.

These examples, while by no means complete, show how general the given type of reaction is, and that many of the apparently different groups of reactions of organic chemistry may be classed together and treated from one general point of view. Some general relations may be developed from these equations. The formation of certain products in any given case depends as stated repeatedly upon equilibrium relationships, velocities of the different reactions, and concentrations of the various substances involved. Taking any one set of reactions, it would be possible to develop regularities with regard to various groups present

in the reacting molecules and the products obtained. To attempt to do this here would lead too far from the main questions which it is desired to present. At the present time, comparable quantitative data with regard to the relative velocities of various reactions are not at hand. In fact, quantitative measurements of very few organic reactions are available, so that it is evident that such a comparison of the constitutional factors upon which the formation of certain sets of products in reactions apparently dissimilar but fundamentally belonging to the same type, is not possible at present. This however does not apply to the possibility of such studies in isolated groups of compounds. For one thing, it is only necessary to refer to Holleman's work on the substitution derivatives of benzene and benzene derivatives, to indicate the nature of the work which may be done in systematizing such reactions. The velocities of esterification of substituted acids and alcohols also offer a large field where much systematic work has already been done and many new and interesting relations have been developed.

There is, however, one set of relations which appears of interest in comparison with reactions of inorganic chemistry. It will have been noticed that in the general reaction

$$BX + HA = BA + HX,$$

the velocities of the reactions of the hydrogen compounds, HA, vary with the character of A just as do the strengths or ionization constants of organic and inorganic acids. It has been customary for some years now to attribute the reactions of many inorganic substances in solutions to the presence of ions, and the primary reason for the reactions and their great velocities to certain properties of the ions. In Chapter III it was shown in the development of the theories of the structures of acids, how the ionic theory played an important part in the evolution of the subject,

and that at present, the view of acids is based upon an outgrowth of the ionic theory and included in the modern views of Werner. Similar relations may be shown to hold for organic reactions where there has been no evidence of ionization as the term is accepted in the theory of electrolytic dissociation.

If, in the above general reaction, A of HA represents an alkyl group, the activity of the compound HA is very small ordinarily. By activity in this connection is meant the amount of reaction in a definite time. It is used in a very rough qualitative sense here, as general quantitative comparisons are not possible at present. If, into the alkyl group are introduced in place of the hydrogen atoms acid groups, so-called negative groups, then the activity of the compound increases in the same way that the ionization constant or strength of an acid in aqueous solution is increased when similar groups are substituted for the hydrogen atoms of the $\alpha$-carbon atom of the acid. In the former case however, ionization according to its present definition need not be apparent. If HA represents an aromatic hydrocarbon, the introduction of these negative groups exerts an opposite effect to that which is noted if they are introduced into an aliphatic hydrocarbon, the former being especially marked when the negative group is in the ortho or para position to the H of HA. On the other hand, with the so-called positive groups OH, $NH_2$, OR, etc., in the ortho or para position to the H of an aromatic HA, the HA corresponds in reaction velocity, etc., to a stronger or more highly ionized acid, while if HA is an aliphatic hydrocarbon the groups have the opposite effect. If B in BX represents an aromatic group such as $(C_6H_5CH) = O$,
(B)
then the $NO_2$ group for example will make the base (as BX may be considered) more active, corresponding to the greater ionization constants of bases. It has been observed,

with reference to the explanation of the mechanism of the reactions, that the readiness of formation of addition compounds in general increases with the strength of the acid (cf. J. Kendall and others).

The advantage of classifying reactions of organic chemistry in the given manner also becomes apparent in connection with such reactions as the decomposition of ketones by alkalies, the "acid" decomposition of acetoacetic ester, the decomposition of acids into hydrocarbons and carbon dioxide, the hydrolysis of tetranitromethane to form trinitromethane, etc. They may also be classed together as the same type of so-called "double decomposition" reaction. It is also evident from this point of view that esters may be decomposed with benzene in an analogous manner to their hydrolysis by water. The relation between aldol condensation, esterification, etherification, etc., is brought out. Again, a point of similarity to inorganic reactions is the effect of the catalyst. It is well known that different solvents influence the electrolytic dissociation of inorganic acids, for example, to different extents. A similar phenomenon is observable in these double decomposition reactions. It is found, in the type equation, that when A is aryl and B is alkyl, that aluminium chloride, sulfuric acid, and zinc chloride act as good catalysts, or in other words, that HA and BX are highly active, corresponding to large ionization in inorganic reactions. On the other hand, if A is aliphatic in nature, it appears that very often alkalies are superior to acids as catalysts, alkalies, amines, and alcoholates being used, as for example, in the aldol condensation. This corresponds to a change in the solvent with different substances in order to obtain a greater degree of activity of the reacting substances.

The statement has already been made in the preceding pages that the present definition for ionization is inadequate. At present a compound in solution is considered to be in

the ionic condition when it conducts the electric current if placed between two electrodes of different potentials. To emphasize more fully the probability that the conception of ionization is not altogether satisfactory, a few reactions may be considered in more detail. The hydrolysis of an inorganic salt is explained by the ionic theory as follows:

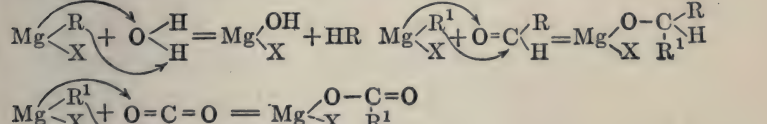
$$\begin{array}{l} MeX \rightleftharpoons Me^{+} + X^{-} \\ HOH \rightleftharpoons OH^{-} + H^{+} \\ \quad\quad\; \downarrow\uparrow \quad\quad \downarrow\uparrow \\ \quad\quad MeOH \quad HX \end{array}$$

If HX is a weak acid (slightly ionized) then the $H^+$ from the $H_2O$ will remove the $X^-$ as HX in solution, increasing the concentration of the $Me^+$ and $OH^-$, and resulting in the hydrolysis of the salt. If the MeOH is a weak base then the $OH^-$ from the $H_2O$ will remove $Me^+$ from solution and cause hydrolysis. It is assumed in each case that the salt MeX is highly ionized. If in the first case, HX is insoluble and in the second MeOH is insoluble, hydrolysis of the salt will take place as well. The $OH^-$ or $H^+$ concentrations may be increased by the addition of alkali or acid to the solution of the salt. A specific example may be taken, namely:

$$MgCl_2 + 2HOH = Mg(OH)_2 + 2HCl.$$

This reaction takes place especially if KOH is used instead of HOH, since the concentrations of the various ions at the equilibrium condition of the system are such that the solubility product of the $Mg(OH)_2$ is exceeded. If, however, in place of $MgCl_2$, MgRCl is used, that is to say the Grignard reagent, it will be observed that this compound is decomposed more rapidly by the HOH than is the $MgCl_2$. This reaction is generally considered only from the double decomposition standpoint, the resultants and reactants, in organic chemistry, and is not considered from the ionic standpoint. It is impossible to state whether this substance is ionized in a water solution since it is immediately

decomposed. But in ether it does conduct the electric current (J. M. Nelson and W. V. Evans, Jour. Amer. Chem. Soc. *39*, 82 (1917)), but up to date the nature of the ions is uncertain. The reaction with water is hydrolysis and very likely of similar character to the decomposition of the $MgCl_2$. $MgRX + 2HOH = Mg(OH)_2 + RH + HX$ or $MgRX + HOH = MgOHX + RH$. With these equations it is still possible to consider the same explanation, namely ionic, for the decomposition of the Grignard reagent and of the magnesium chloride. It is well known, however, that the Grignard reagent is used to a great extent in organic syntheses in which it is decomposed by oxygen compounds other than water. Thus, aldehydes, ketones, carbon dioxide, cyanides, etc., stated in organic chemistry to contain unsaturated groups, react with the MgRX. The simplest way to account for the reactions is to compare them with the hydrolysis of the RMgX by water.



This way of indicating the changes makes it evident that the aldehyde and the carbon dioxide act in the same way as the water, but the aldehyde and the carbon dioxide are not considered as electrolytes and hence the ionic explanation seems to be inadequate.

The classifications and general relations developed here together with evidence presented in a paper published some years ago (K. G. Falk and J. M. Nelson, Jour. Amer. Chem. Soc. *37*, 1732 (1915)) apparently justify the conclusion that the changes occurring in chemical reactions do not depend upon the electrolytic dissociations of the reacting substances. The chemical changes are accompanied very often by electrolytic dissociation phenomena, but the latter

parallel the former (or vice versa) and do not necessarily precede or cause them. For organic reactions it need not be necessary to present further evidence in this connection. With inorganic reactions, however, the question appears not to be so simple. The theory of electrolytic dissociation does not necessarily postulate that only ions react. For some time after the theory of electrolytic dissociation was proposed, it was attempted to apply the theory to every possible case where there was the slightest possibility of an explanation based upon it. In recent years the trend of thought has taken a different turn, and the explanations of certain reactions, which at one time had been assumed to be purely ionic in character, considered the un-ionized molecules as also taking part in the reactions. The first steps in this development were taken by G. Senter (J. Chem. Soc. *91*, 467 (1907)) and by S. F. Acree (Am. Chem. J. *37*, 410; *38*, 258 (1907)), and these have since been followed by S. Arrhenius, G. Bredig, H. C. S. Snethlage, H. Goldschmidt, H. M. Dawson, A. Lapworth, H. S. Taylor, J. Stieglitz, and others, who favor the view that both ionized and un-ionized molecules are active in chemical changes even in aqueous solution and present evidence bearing on the question.

According to the views presented here, electrolytic dissociation is not the forerunner of chemical reactions and in fact chemical reactions do not depend upon the presence of ions as postulated in that theory. Certain physical properties of substances, which, early in the history of the electrolytic dissociation theory, were considered to be dependent upon ionization, have since been shown to be independent of it. Thus, the color of a salt in solution was assumed to be made up of the different colors of the ions and the un-ionized molecule. Later work showed that ionization changes do not affect the color of the substance. Reference may be made here to a detailed review of these relations published by J. Lifschitz (Sammlung chemischer

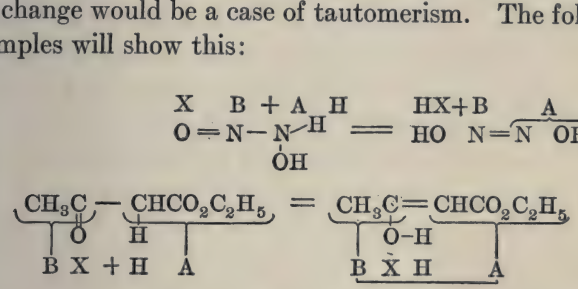
und chemisch-technischer Vorträge, Vol. 21, Nos. 5–7, p. 175 (1914)). The explanations advanced at different times with regard to the color changes of indicators illustrate these views very well. Ostwald in 1894 ("Die wissenschaftlichen Grundlagen der analytischen Chemie," p. 104) attributed the different color of an indicator in acid or alkaline solution to the different colors of the ions and un-ionized molecules. If the indicator substance itself was an acid, the color in acid solution would be that of the un-ionized molecule, while in alkaline solution the color would be that of the negative ion. If the indicator substance was a base, the color in alkaline solution would be that of the un-ionized molecule, in acid solution that of the positive ion. This theory was shown not to be general enough to include the observed phenomena, and was replaced by the "chemical" theory first suggested (for phenolphthalein) by Bernthsen and developed by J. Stieglitz (Jour. Am. Chem. Soc. *25*, 1112 (1903)) and especially by A. Hantzsch Ber. *39*, 1090 (1906) and numerous articles since) who showed the ionic theory of indicators to be highly improbable. The present view considers every change in color of an organic substance to be due to an intramolecular rearrangement. Indicators form a special group in so far as the intramolecular rearrangements in their case are tautomeric in character and include, therefore, in most cases the shifting of a hydrogen atom in passing from one form to the other. The production of ions is secondary in the tautomeric changes, and if the ions are colored, it is because the un-ionized molecules from which they are derived are colored. The equilibrium between the tautomeric forms of a substance depends upon a variety of factors, such as solvent, temperature, small amounts of certain added substances such as acids or bases, etc. Hantzsch has shown the important part played by solvents in affecting the equilibrium (and therefore the color change)

between the tautomeric forms of some indicators (Ber. *48*, 158 (1915)). Such actions take place with indicators in solution in practical titrations where the indicator substance is present in such small concentration that the color change which accompanies the transformation of one tautomer into the other is very marked with the relatively small amount of added substance necessary to produce it (cf. A. A. Noyes, Jour. Amer. Chem. Soc. *32*, 815 (1910)). Other changes of conditions may be considered similarly for the indicators as a special class of tautomeric substances. In general, it may be stated that the various factors which influence the equilibrium between tautomers also influence the equilibrium between the different tautomeric forms of indicators, and that the question of the electrolytic dissociation of the indicator substances does not enter into the theory of their color changes as assumed in the earlier theory, although it appears to be connected with one of the factors involving the sensitiveness.

It is evidently possible to extend this method of treatment to other reactions. No more will be taken up at present, but the view will be emphasized that chemical reactions need not be considered to depend upon electrolytic dissociation. With the atoms in a molecule all carrying electric charges, certain properties of a solvent make some of these charges evident to experimental methods, while certain, perhaps very often the same, properties of the solvent increase the extent or rate of a reaction. These phenomena are independent of each other but both dependent upon the solvent, or possibly some other underlying cause. Many, if not all, of the changes which have been considered heretofore as metatheses, involve, without doubt, primary addition and subsequent decomposition or splitting off in various ways of the reacting molecules.

The question of tautomerism and the factors influencing it may be considered further in the same way as organic

reactions in general. To illustrate: In the general type reaction $BX + HA = HX + BA$, if instead of considering both molecules to be separate entities, they are considered to be components of a single more complex molecule, then the change would be a case of tautomerism. The following examples will show this:



Since A is an aliphatic "negative" group in the second example, the compound is more "active" and shows tautomerism more readily. The factors which influence the activity of organic compounds as pointed out before influence the activity of these compounds enabling them to show the tautomerism or to exist more readily in mutually convertible forms. Tautomeric changes may therefore be included in this group of organic reactions and the same laws and relations apply to all.

The classifications and explanations of the mechanisms of reactions which have been developed have been illustrated by means of qualitative examples. Innumerable examples of the reactions might be cited but unfortunately the quantitative data at hand are too few to permit of general conclusions. The possibilities in the way of different products being formed also complicate the quantitative study with many organic reactions.

A beginning has been made in the problem of obtaining quantitative measures of relative stability for a number of organic compounds. Reference may be made to several papers by C. G. Derick bearing on this question (Jour. Amer. Chem. Soc. *32*, 1333 (1910); *33*, 1152 (1911)).

Some of his conclusions from his experimental work may be given:

In his first paper he takes up the question of stability of isomeric compounds which rearrange to form more stable substances to a practically irreversible extent under the given conditions. Quantitative data are supplied for a series of such changes. The rearrangement of a number of acids and bases to more stable configurations was given. The stability of these compounds toward ionization was used as a measure. The equation $A = RT \log_e K$ was made use of, A representing the free energy of ionization; R, the gas constant; T, the absolute temperature; and K, the ionization constant. The free energy of ionization of acids and of bases is shown as the change in free energy of the reactions $HA \rightleftharpoons H^+ + A^-$ for acids and $ROH \rightleftharpoons R^+ + OH^-$ for bases (omitting the part played by the solvent), when the initial and final substances are at unit concentration. It is evident, therefore, that the free energy of ionization is directly proportional to the natural logarithm of the ionization constant, and that to determine the relative stabilities of two acids (or bases) in terms of the free energy of ionization, it is only necessary to compare the logarithms of their ionization constants. Since an acid is more stable toward ionization when it possesses a smaller ionization constant or smaller free energy of ionization, the stability toward ionization of an acid is greater the smaller its ionization constant. The exact measures of stability are given by the logarithms of these ionization constants. Derick gives the results of a number of isomeric organic acids, and draws some general conclusions with regard to their structures and relative stabilities toward ionization. For example, for tetrahydrobenzenecarboxylic acids, he finds that "whenever the unsaturation is $\Delta^2$ with respect to a given carboxyl group true rearrangements of the non-reversible type are possible" and also "the compounds from which Thiele

deduced his theory of partial valence, as well as other acids which obey the same rule, must be compounds which are formed with weak reducing agents involving small energy changes and where the speed of reaction is small so that compounds result which are very unstable toward ionization, and therefore toward rearrangement." In addition to these quantitative results, a number of rearrangements are grouped in Derick's first paper under various headings. These relations are, however, only qualitative in character.

In a second series of papers, Derick goes farther and studies the "polarity of elements and radicals measured in terms of a logarithmic function of the ionization constant." This is evidently the direction in which advance is to be expected, a study of the action of various groups on the equilibria of certain reactions in terms of affinity changes. The following definitions are given by Derick:

1. An element or radical possesses positivity if, when it is substituted for a hydrogen of water, it increases the hydroxyl ionization. It is therefore said to be positive.

2. An element or radical possesses negativity if, when it is substituted for a hydrogen of water, it increases the hydrogen ionization. It is therefore said to be negative.

Water is used as the standard for determining the polarity of various groups. The relative free energies toward ionization of the various substances are used to determine the relative stabilities, and in this sense the classification is limited. It is however useful and important as a comparison of the stabilities toward a certain transformation and giving a measure of the effect on a definite reaction of different groups. A table is given of a number of these ionization constants ($K_a$ and $K_b$ for acidic and basic ionization) and the free energy values ($RT \log_e K$). In the succeeding papers (and also later (with O. Kamm) in the Jour. Amer. Chem. Soc. *39*, 388 (1917)) Derick takes up a number of reactions and discusses the effects of various

groups upon the stabilities of the reactions. No attempt will be made to discuss in detail the applications and conclusions of Derick here, but the reader is referred to his papers for a careful study of the work. This is perhaps the first systematic attempt to study in a quantitative way the affinity relationships of a large number of organic compounds, and to obtain exact data with regard to the effects of different groups on the equilibrium constants and therefore the stabilities in certain reactions in various molecules. The importance of this work must therefore be emphasized as marking a beginning of the systematic quantitative study of reactions such as have been given in these chapters, where for lack of sufficient data, only the qualitative aspects could be presented.

## CHAPTER VIII.

### OLEFINS AND THEIR REACTION PRODUCTS.

It was stated in the preceding chapters that the reactions of organic chemistry may be treated from the same point of view as the reactions which have been classed under inorganic chemistry. The same general relations apply to all reactions in chemistry, even if, because of convenience in grouping or presentation, they have been classed separately. A certain justification for the separate treatments is found in the fact that characteristic phenomena are predominant in some reactions which are more in the background in other reactions. Even if this is true, it must be remembered that the same underlying principles apply to all reactions and that the laws or generalizations of chemistry must necessarily hold for all chemical phenomena, and not one set of laws for some compounds and another set for other compounds. At most, no sharp dividing line is ever supposed to exist between the two, but only a gradual transition set of compounds or reactions, which may belong to one group or to the other. The point of view to be emphasized is again similar to the point of view presented in Chapter I, in which it was shown that two kinds of valence, polar and non-polar, were unnecessary in the development of atomic valence structures.

In taking up some of the reactions of organic chemistry, the group of compounds which come to mind as being very reactive, reactive in the sense of reacting rapidly with a large number of different reagents, is the olefins. This property of reacting with many compounds is well brought out for these compounds in the term "unsaturated hydrocarbons." The use of the term "unsaturated" was applied in Chapter V to other compounds which formed addition

compounds also. Ammonia was used there as a typical example. Because of the general point of view which is emphasized here, the comparative study of the unsaturated properties of the olefins and of ammonia will be of value.

The combination of olefins with acids to form esters, etc., is strikingly similar to the combination of ammonia and acids to form salts. In the great majority of these compounds one molecule of the olefin or ammonia combines with one equivalent of the acid. The reaction is also reversible in both series. Designating the olefin by the symbol *En*, (ethylene as example), the following reactions may be given.

$En + HCl = EtCl$ (Et denoting Ethyl),

$En + H_2O = EtOH$ (Water taking the part of the acid),

$C_5H_{10} + HO_2C.CCl_3 = C_5H_{11}O_2CCCl_3$,

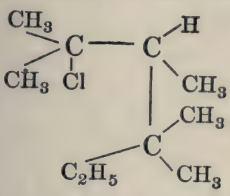
$En + H_2SO_4 = EtHSO_4$,

$CH_3CO_2Et = En + CH_3CO_2H$

(A. Oppenheim and H. Precht, Ber. *9*, 325, (1876).

Esters may be regarded as the olefinates of acids, just as ammonium salts can be looked upon as the ammoniates of acids. Just as ammonia combines with salts such as $PtCl_4$, $CaCl_2$, etc., to form ammoniates, so may olefins combine with salts to form olefinates. Compounds of this last type have not been studied extensively, but the following may be mentioned: $(CH_3)_2C : CHCH_3.2ZnCl_2$ (from isobutylene and zinc chloride) [J. Kondakow, J. pr. Chem. (2) *48*, 474 (1893)]; $C_2H_4.PtCl_4$ [V. Meyer and P. Jacobson, Lehrbuch der organischen Chemie, Vol. 1, p. 832 (1907)]; etc.

So-called "anomalous" olefinates, which contain a different proportion of acid or salt than the 1 : 1 ratio are also known. The zinc chloride compound just given is an example; partially saturated polyolefins, such as the mono-

halogen addition products of terpenes as menthadienes, belong to this group; ethyl ether may be looked upon as a diolefinate of water; the compound $(CH_3)_2O.C_2H_4$ [G. Baume and A. F. O. Germann, C.r. 153, 569 (1911)] may be written $(CH_2)_4.H_2O$; $C_2H_4.7H_2O$ [R. de Forcrand, C.r. *135*, 959 (1902)] is an example; a complex alkyl halide such as  may be formed by the combination of several molecules of simpler olefins and one molecule of hydrogen chloride (Meyer and Jacobson, pp. 833, 836); etc.

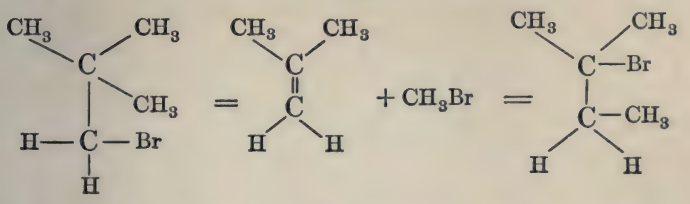
Mixed addition compounds containing olefins have also been described; for example, $FeCl_2.C_2H_4.H_2O$ [J. Kachler, Ber. *2*, 510 (1869)]; $FeBr_2.C_2H_4.H_2O$ [C. Chojnacki, Z.f. Chem. 1870 p. 419)]; $(CH_3)_2O.NH_3$, an olefinate and ammoniate of water, etc.

These reactions show the similarity between the olefins and ammonia, and that the common property of unsaturation in both leads to the formation of analogous products.

The simplest compounds which are formed from the olefins are the alkyl halides, which correspond to the ammonium halides. There is at present no direct experimental evidence of the action of catalysts in their formation, but in their dissociation into olefin and hydrogen halide, aluminium chloride, zinc chloride, etc., affect the rate of reaction greatly [P. Sabatier and A. Maihle, C.r. *138*, 407 (1904); *141*, 238 (1905)]. This shows itself more particularly in the lower temperature necessary for their rapid dissociation. The alkyl chlorides dissociate more readily than do the bromides, and these more readily than do the iodides. Although no exact quantitative data regarding the

velocities and equilibria of these reactions are at hand, they may be considered to be analogous to the relative degrees of dissociation of the ammonium halides studied by A. Smith and co-workers [Jour. Amer. Chem. Soc. *37*, 38 (1915)]. The action of certain substances such as alkalis in these reactions will be taken up later in this chapter.

A further relation of the alkyl halides may be mentioned. Under the same conditions, the primary halides dissociate more readily than the secondary, and the secondary more readily than the tertiary (Sabatier and Maihle, l.c.). In the study of this reaction, no statement was made as to the probable equilibria. [It will have been noticed that in the discussion of organic reactions, the experiments often are not definite or quantitative. This leads to uncertainty in the theoretical treatment, as to whether a ready formation of a compound refers to the velocity under certain conditions or to the amount present under equilibrium conditions. Careful regulation of conditions and quantitative working are essential for the further development of the science of reactions included in organic chemistry.] It is possible to conceive of the tendency of the *n*-alkyl halides going over into the *iso* on boiling, or of the formation of isopropyl benzene from *n*-propyl chloride and benzene by the Friedel-Crafts reaction, as due to the different equilibria of the olefin and hydrogen halide with different sets of products (*normal, iso,* and *tertiary* halides); the one which is found experimentally depending upon the conditions of the various equilibria, or the relative velocities of the reactions. Connected with this is the reaction in which hydrogen halide is added to an olefin, the halogen being finally combined mainly with the carbon with least hydrogen; that is to say, to form the tertiary compound preferably, secondarily the iso-compound [A. Michael Ber. *39*, 2138 (1906)]. Another example of the same kind is the formation of 2-brom-, 2, 2, 1, trimethyl ethane by heating 1-brom-, 2, 2, 2-trimethylethane



[L. Tissier, Ann. de chim. et de phys. (6) *29*, 359, 361, 364 (1893)].

A general method, used very often practically, for the preparation of olefins consists in the action of an alcoholic solution of potassium hydroxide on an alkyl halide. This reaction is analogous to the production of ammonia from ammonium chloride and an aqueous solution of an alkali. The equations for the latter are generally given as the following:

$$NH_4Cl = NH_4^+ + \bar{C}l, \quad (1)$$

$$KOH = K^+ + \bar{O}H, \quad (2)$$

$$NH_4^+ + \bar{O}H = NH_4OH, \quad (3)$$

$$NH_4OH = NH_3 + H_2O. \quad (4)$$

Omitting the action of water in these equations, (1) and (2) represent the ionization in solution. Equation (3) shows the equilibrium between $\dot{N}H_4$ and $\bar{O}H$ ions and un-ionized $NH_4OH$. Equation (4) shows the equilibrium between the last named substance and its dissociation products, ammonia and water. Since the last reaction takes place to a great extent to form the products of dissociation, there will be a progressive action to form ammonia, especially if it is removed from the sphere of action by heat or in some other way, or if the concentration of $\bar{O}H$ is very large, until, finally, all the ammonium chloride has reacted to form ammonia. If the same explanation were applicable to the alkyl halide, the following equations would hold:

$$C_2H_5Cl = C_2H_5^+ + \bar{C}l,$$
$$KOH = K + \bar{O}H,$$
$$C_2H_5^+ + \bar{O}H = C_2H_5OH,$$
$$C_2H_5OH = C_2H_4 + H_2O.$$

This explanation is not satisfactory for olefins. In the first place, no evidence is at hand indicating that the alkyl halides ionize. One of the arguments advanced to meet this criticism is that the solvent in the case of the formation of the olefin is not water and therefore the two cases are not comparable. If water were used as the solvent, the solubility of the alkyl halide would be so small that ionization in solution could not be detected by any of the present methods. On the other hand, very small concentrations of ions can be detected experimentally. Most chemists, therefore, do not attempt to explain the reactions of alkyl halides on the ionization basis. The two reactions, the formation of ammonia and the formation of olefins, consequently are considered to be quite different.

If the formation of ammonia from ammonium salts is considered from the addition-dissociation and displacement point of view, the two reactions become analogous. Upon this basis the formation of ammonia may be indicated as follows:

$$NH_4Cl + nH_2O = \begin{bmatrix} HCl \\ NH_3 \\ (H_2O)_n \end{bmatrix}$$

Solution of the ammonium chloride. ($NH_4Cl$ might be written for $NH_3$, HCl.)

$$\begin{bmatrix} HCl \\ NH_3 \\ (H_2O)_n \end{bmatrix} + \begin{bmatrix} KOH \\ H_2O)_m \end{bmatrix} = \begin{bmatrix} HCl \\ NH_3 \\ (H_2O)_{n+m} \\ KOH \end{bmatrix}$$

$$= \begin{bmatrix} KCl \\ (H_2O)_p \end{bmatrix} + \begin{bmatrix} NH_3 \\ (H_2O)_{n+m-p} \end{bmatrix}.$$

Or it may be represented according to the general type reaction (chapter 5) as follows:

$$[(H_2O)_xNH_4Cl] + KOH = [(H_2O)_xNH_4KOH]Cl$$
$$= NH_3 + (H_2O)_{x+1} + KCl.$$

Similarly for the alkyl halides; in aqueous solution the equations would be:

$$[(H_2O)_yC_2H_5Cl] + KOH = [(H_2O)_yC_2H_5KOH]Cl$$
$$= C_2H_4 + (H_2O)_{y+1} + KCl$$

and in alcoholic solution:

$$[(C_2H_5OH)_zC_2H_5Cl] + KOH = [(C_2H_5OH)_zC_2H_5KOH]Cl$$
$$= C_2H_4 + (C_2H_5OH)_z + H_2O + KCl.$$

It is true that this explanation appears to be more complicated than the ionic explanation, but it has in its favor the fact that it is more general, and unquestionably represents more nearly the mechanism involved.

For most purposes it is not necessary to write the reactions in such a complicated way, the following being sufficient:

$$KOH + C_2H_5Cl = \begin{bmatrix} KOH \\ HCl \\ C_2H_4 \end{bmatrix} = KCl + C_2H_4 + H_2O,$$

$$KOH + NH_4Cl = \begin{bmatrix} KOH \\ HCl \\ NH_3 \end{bmatrix} = KCl + NH_3 + H_2O.$$

When potassium hydroxide is dissolved in alcohol, there is likely to be some potassium ethoxide, $KOC_2H_5$, formed. (It is incorrect to name compounds of this type alcoholates, since alcoholates correspond to hydrates, while these compounds correspond to hydroxides.) There is, therefore, a possibility of the formation of ethers when alkyl halides are treated with an alcoholic solution of potassium hydroxide.

$$C_2H_5Cl + KOC_2H_5$$
$$= \begin{bmatrix} C_2H_4 \\ HCl \\ KOH \\ C_2H_4 \end{bmatrix} = \begin{bmatrix} C_2H_4 \\ H_2O \end{bmatrix} \text{ (or } C_2H_5OH) + KCl + C_2H_4$$
$$= \begin{bmatrix} C_2H_4)_2 \\ H_2O \end{bmatrix} \text{ (or } (C_2H_5)_2O) + KCl, \text{ etc.}$$

Another very interesting point in connection with the reactions of the alkyl chlorides, bromides and iodides, is the fact that the iodides show a tendency to give a larger yield of olefin than do the chlorides in the presence of alkali [A. Lieben and A. Rossi, Lieb. Ann. *158*, 164 (1871)]. This is the opposite to what would have been supposed from the behavior of the halides in the presence of catalysts such as aluminium chloride. Furthermore, the chlorides yield ether more readily than do the corresponding bromides or iodides [M. Wildermann, Z. phys. Chem. *8*, 661 (1891); and S. Brussow, Ibid. *34*, 129 (1900)].

All of these reactions depend very likely upon the relative velocities of the various possible dissociations of the intermediate addition compounds under the given conditions.

The reason why ordinarily mixed ethers of the type $C_2H_5ONH_4$ are not obtained is that they undergo dissociation at such low temperatures. If the alcohol-ammonia mixture is cooled sufficiently, these compounds are formed, and may be isolated. For example, $CH_3OH.NH_3$ and $(CH_3)_2O.NH_3$ (G. Baume and co-workers, J. de Chim. Phys. *12*, 216, 225 (1914)) belong to this type.

A reaction similar to that of ammonia and of the amines is that by which olefins may be alkylated to form olefins containing a greater number of carbon atoms. Thus, amylene treated with methyl iodide yields hexylene and heptylene [(M. Eltekoff, Ber. *11*, 412 (1878); J. Lermontoff, Lieb. Ann. *196*, 116 (1879)].

$$C_5H_{10} + CH_3I = C_6H_{12} + HI,$$
$$C_5H_{10} + 2CH_3I = C_7H_{14} + 2HI.$$

The alcohols may be regarded as a group of compounds similar to the alkyl halides in being olefinates of water in place of acid, just as ammonium hydroxide is an ammoniate of water. The formation of an alkyl halide from an alcohol may therefore be looked upon as the displacement of water by hydrogen halide.

$$[C_2H_4.H_2O] + HCl = [C_2H_4.HCl] + H_2O,$$
$$[NH_3.H_2O] + HCl = [NH_3.HCl] + H_2O.$$

The olefinates of water differ from those of the hydrogen halides in that the tertiary alcohols appear to lose water to form the olefins more readily than do the secondary, and the secondary more readily than do the primary. This is the opposite to the order observed with the halides, but whether this difference refers to the actual thermodynamic stability or to the relative velocities under certain conditions is not definite.

The formation of olefins from alcohols is similar to the formation of ammonia from ammonium hydroxide:

$$[C_2H_4.H_2O] = C_2H_4 + H_2O,$$
$$[NH_3.H_2O] = NH_3 + H_2O.$$

The olefin formation is influenced very much by the presence of other substances which act as catalysts. Sulfuric acid is one of those most commonly used in this reaction. The efficiency of the sulfuric acid in this reaction is often connected with its tendency to combine with water, or its dehydrating property. In the final products, it is true that the elements of water have been removed from the alcohol, but the mechanism of the reaction is unquestionably not so simple. The continuous formation of ethylene by running ethyl alcohol into warm sulfuric acid; the formation of alcohol from an olefin and dilute sulfuric acid [A. Butleroff, Lieb. Ann. *180*, 245 (1876)]; the formation of alcohol from olefin and concentrated sulfuric

acid as well as the saponification of the ester formed;—all speak against such a simple interpretation. Since ethyl alcohol and sulfuric acid, or olefin and sulfuric acid, form ethyl sulfuric acid, Et $HSO_4$, which breaks down, on heating, into olefin and the acid, most textbooks state that the first step in this reaction is the formation of this ester. According to the general theory of addition reactions advanced in this book, the intermediate compound would be more complex, and the ethyl sulfuric acid itself would be one of the products of the dissociation. A number of equilibria may be given to represent the possible dissociation products. This list is not complete but will indicate the possibilities of the reaction.

$$\left[\begin{matrix}(En)_a \\ (H_2O)_b \\ H_2SO_4\end{matrix}\right] \begin{matrix} \rightleftharpoons a\ EtOH + H_2SO_4 + (b\text{-}a)H_2O & (1) \\ \rightleftharpoons En\ H_2SO_4 + b\ H_2O + (a\text{-}1)En & (2) \\ \rightleftharpoons a\ En + H_2SO_4\ (H_2O)_b & (3) \\ \rightleftharpoons a\ En + bH_2O + H_2SO_4 & (4) \\ \rightleftharpoons \frac{a}{2}En_2\ H_2O + H_2SO_4 + (b\text{-}\frac{a}{2})\ H_2O & (5) \\ \rightleftharpoons En_2 + (a\text{-}2)\ En + H_2SO_4 + bH_2O & (6) \end{matrix}$$

Equilibrium (1) represents the reaction between ethyl alcohol, sulfuric acid and water to form the intermediate product; (2) the formation of the ethyl sulfuric acid; (3) the formation of ethylene; (4) the formation of ethylene and the simultaneous giving off of water; (5) the formation of ethyl ether; (6) the formation of a polymer of ethylene. All of these reactions have been observed experimentally, and the products actually obtained under given conditions, depend upon these conditions and the principles of the law of mass action. This list served to indicate the possibilities for the quantitative study of a common reaction presumably well-known.

If a different catalyst were used in the above reaction, while the various equilibria would be identical in principle, the products actually obtained under any set of definite

conditions might be different due to the specific action of the catalyst on the different equilibria.. The action of zinc chloride may be cited. With trimethyl ethylene, the compound $(CH_3)_2C : CH\ CH_3.2ZnCl_2$ has been isolated. With water it gives dimethylethyl carbinol, $(CH_3)_2.C(OH).CH_2.CH_3$; with hydrogen chloride, tertiary amyl chloride; if heated alone, diisoamylene [J. Kondakow, J. pr. Chem. (2) *48*, 475 (1893)]. Sulfuric acid and isoamylene under suitable conditions yield diisoamylene also. This polymerization reaction is used commercially in the formation of synthetic rubber from the octadiens. The specific action of the particular catalyst employed is shown also by the fact that *iso*-propyl bromide dissociated at the temperature of boiling amylene in the presence of asbestos, while the *n*-bromide did not. [D. Konowalow, Ber. *18*, 2808 (1885).]

Although liquid ammonia is an associated liquid [E. C. Franklin and C. A. Kraus, Amer. Chem. J. *21*, 14 (1899)] similar polymerization reactions have not been observed with ammonia or amines.

The acetylene hydrocarbons may be studied from the same point of view as the olefin hydrocarbon. They only differ in the degree and amount of unsaturation.

It was shown that alkyl halides may be formed from olefins and acids and may be looked upon as salts of the hydrogen halides, or, as organic chemists have been in the habit of calling such salts, as esters of the halogen acids. In speaking of the alkylation of olefins, it was pointed out that alkyl halides add to olefins, the alkyl radical playing the same part as the hydrogen of the hydrogen halide in such reactions. Zinc chloride facilitated the addition of the alkyl halide to the olefin as J. Kondakow [J. pr. Chem. *54*, 452 (1896)] showed. He described the reaction as follows:

$$(CH_3)_2C : CH\,CH_3 + Cl.C(CH_3)_2(C_2H_5) + ZnCl_2 = (CH_3)_2C(Cl) - CH\,CH_3\,C(CH_3)_2C_2H_5 + ZnCl_2.$$

As he did not examine the intermediate addition compound of the three reacting components, but treated the mixture directly with water, removing the zinc chloride, he could not determine the action of the latter. He did notice, however, that when the olefin-zinc chloride addition compound was treated with hydrogen halide, the latter replaced the zinc chloride and formed the corresponding alkyl halide [J. pr. Chem. *48*, 475 (1893)]. At higher temperatures, large amounts of the polymerized olefin were formed. These various reactions can be accounted for on the basis of various equilibrium equations.

Many other salts have properties similar to those of zinc chloride. Thus, G. Gustavson [J. pr. Chem. (2) *34*, 161 (1886)] found that aluminium bromide formed a compound with butylene, and the use of mercury salts for the hydration of olefins and acetylenes, etc., may be quoted. For the further discussion of the addition of alkyl halides to olefins, the reader is referred to the chapter on the Friedel-Crafts reaction. Just as amines and ammonia react with acid anhydrides and acid chlorides, so do the olefins. J. Kondakow [Ber. *27*, Ref. 309, 941 (1894)] was able to bring about the addition of these substances to olefins in the presence of zinc chloride, etc. The external conditions must, however, be regulated carefully in order to obtain the desired products; that is to say, to have the intermediate addition compound dissociate along the lines of the necessary equilibrium.

Since some of the oxides of nitrogen may be looked upon as similar in constitution to anhydrides of oxygen acids, it is readily understood why addition products can be obtained from these oxides and the olefins. When nitrogen trioxide

is passed into a cooled ethereal solution of trimethylethylene, amylene nitrosonitrite, $(CH_3)_2\,C(ON)-CH(NO)CH_3$, is formed.

A compound such as this is subject to tautomeric change and polymerization. For further details concerning these reactions, the reader is referred to books on the chemistry of the terpenes.

When acids add to olefins, the olefinates formed may be termed salts or esters. The formation of olefinates is therefore one form of esterification similar in principle to the formation of ammonium salts and of hydrates of acids or oxonium salts. Similarly, the hydration of olefins to form alcohols and ethers really belongs to the same class of reactions, alcohols and ethers from this point of view being esters of the acid water. So far the olefinates, the alkyl halides, have been considered in some detail. According to the terminology in general use, these are esters formed from organic alcohols and inorganic acids, the hydrogen halides. The esters formed with organic acids will now be taken up in the same way first, and then the general question of esterification will be considered.

The formation of esters with organic acids has been studied in detail with the olefin, amylene. This is doubtless due to ease of manipulation and experimental technic in general. The results with this olefin may be carried over to other olefins, and the general principles will hold for all.

D. Konowalow [Ber. *18*, 2808 (1885)] showed that gaseous amyl acetate dissociated at 180° with appreciable velocity when substances like asbestos, barium sulfate, glass wool, etc., were present. N. Menschutkin [Ber. *15*, 2512 (1882)] had observed that this ester dissociated into amylene and acetic acid, even in the liquid state at a comparatively low temperature, and that the velocity of this dissociation increased as the reaction proceeded. D. Konowalow [Z.

physik. Chem. *1*, 63 (1887)] showed this auto-catalytic action to be due to the increasing concentration of acid which was formed in the reaction, and that the stronger the acid (the more highly ionized in aqueous solution) so formed, the greater its action [Z. physik. Chem. *2*, 6 (1888)]. Thus, the amyl ester of trichloracetic acid dissociated more rapidly than the amyl ester of acetic acid. The addition of hydrogen halide also caused the dissociation of amyl acetate, with the subsequent formation of amyl halide. The equations showing these changes are as follows:

$$\begin{bmatrix} \text{Am} \\ \text{HAc} \\ \text{HX} \end{bmatrix} = \begin{bmatrix} \text{Am} \\ \text{HAc} \end{bmatrix} + \text{HX}$$

$$\begin{bmatrix} \text{Am} \\ \text{HAc} \\ \text{HX} \end{bmatrix} = \begin{bmatrix} \text{Am} \\ \text{HX} \end{bmatrix} + \text{HAc.}$$

$$= \text{Am} + \text{HAc} + \text{HX}$$

W. Nernst and C. Hohmann [(Z. physik. Chem. *11*, 352 (1893)] showed that in the reaction between olefin and acid to form ester, the stability of the ester, as measured by the equilibrium constant

$$\frac{C_{\text{acid}}\, C_{\text{olefin}}}{C_{\text{ester}}} = K$$

increased, and the value of the constant K decreased, with the strength of the acid. Similar conclusions were reached by J. Kendall [J. Am. Chem. Soc. *36*, 1722 (1914)] and others. Nernst and Hohmann also showed that the velocity of formation of amyl trichloracetate from amylene and the acid was proportional to the square of the concentration of the acid. In benzene as solvent, the velocity was greatly increased, because of the association of the acid; in ether, on the other hand, the velocity was less, the acid not being associated in it. At the same time it is probable that the ether and the trichloracetic acid form a complex, indicated perhaps by the following equilibria:

$$\begin{bmatrix}\mathrm{AcOH}\\ \mathrm{AcOH}\end{bmatrix}+n\mathrm{Et_2O}=\begin{bmatrix}\mathrm{AcOH}\\ \mathrm{AcOH}\\ n\mathrm{Et_2O}\end{bmatrix}=\begin{bmatrix}\mathrm{AcOH}\\ a\,\mathrm{Et_2O}\end{bmatrix}+\begin{bmatrix}\mathrm{AcOH}\\ (n-a)\mathrm{Et_2O}\end{bmatrix}.$$

The influence of benzene and ether as solvents on the velocity of the ester formation is similar to their influence on the reaction between triethylamine and ethyl iodide described in Chapter V.

Just as zinc chloride accelerates the reaction between an olefin and water to form the alcohol and the reverse reaction, so also does it accelerate similar reactions in which an acid or an alkyl halide takes the place of the water. J. Kondakow [J. pr. Chem. *48*, 479 (1893)] found that when zinc chloride was added to a solution of trimethylethylene and acetic acid, an addition compound, $C_5H_{10}.ZnCl_2.(HOAc)_3$ crystallized out. Treated with water, this addition compound yielded amyl acetate. By altering the conditions so as to obtain the maximum yield, that is, by isolating this intermediate addition compound, and treating it with water, Kondakow was able to obtain a 20 per cent. yield of ester, although, ordinarily, in the equilibrium mixture containing amylene, acetic acid, and amyl acetate, only 2 per cent. of ester was present (Nernst and Hohmann). If the reaction mixture was allowed to stand for some time before water was added, a considerable amount of diamylene was formed. The reaction may be formulated as follows:

$$x\mathrm{C_5H_{10}}+y\mathrm{HOAc}+z\mathrm{ZnCl_2}$$

$$=\begin{bmatrix}(\mathrm{C_5H_{10}})_x\\ (\mathrm{HOAc})_y\\ (\mathrm{ZnCl_2})_z\end{bmatrix}=a\begin{bmatrix}\mathrm{C_5H_{10}}\\ \mathrm{HOAc}\end{bmatrix}+z\mathrm{ZnCl_2}$$

$$=b\begin{bmatrix}\mathrm{C_5H_{10}}\\ \mathrm{C_5H_{10}}\end{bmatrix}+y\mathrm{HOAc}+z\mathrm{ZnCl_2},$$

$$\begin{bmatrix}(\mathrm{C_5H_{10}})_x\\ (\mathrm{HOAc})_y\\ (\mathrm{ZnCl_2})_z\end{bmatrix}+n\mathrm{H_2O}=\begin{bmatrix}(\mathrm{C_5H_{10}})_x\\ (\mathrm{HOAc})_y\\ (\mathrm{ZnCl_2})_z\\ (\mathrm{H_2O})_n\end{bmatrix}$$

$$=c\begin{bmatrix}\mathrm{C_5H_{10}}\\ \mathrm{HOAc}\end{bmatrix}+d\begin{bmatrix}\mathrm{ZnCl_2}\\ \mathrm{H_2O}\end{bmatrix}.$$

The other equilibria which are possible with these substances are not given. They would be similar to the equilibria in which sulfuric acid is present in place of zinc chloride, which were given on a preceding page. In this reaction, the zinc chloride plays the same part as the extra molecule of acetic acid in the associated acetic acid in the formation of amyl acetate, the only difference being that the zinc chloride addition compound under the conditions of its formation, does not form appreciable amounts of ester, but only when treated with water. A. Béhal and A. Desgrez [C. r. *114*, 676 (1892)] have used this method for the formation of esters of higher olefins.

Since the esters of organic acids are olefinates, it is clear why, in the distillation of esters like the waxes, etc., where a high temperature is necessary, olefins are often formed:

$$C_{15}H_{31}CO_2C_{18}H_{37} = C_{15}H_{31}CO_2H + C_{18}H_{36}.$$

So far esters have been considered only in relation to their formation from olefins and acids. The usual method for preparing esters consists in the action of an alcohol on an acid in the presence of a catalyst. The mechanism of this reaction has been studied extensively in recent years, and all the evidence indicates the formation of intermediate addition compounds in the reaction. The most direct evidence of the existence of such intermediate compounds composed of alcohol, acid, and catalyzing inorganic acid was given by G. Baume and G. P. Pamfil [J. Chim. Phys. *12*, 260 (1914)] and by J. Kendall and J. E. Booge [J. Am. Chem. Soc. *38*, 1712 (1916)]. Kinetic studies by J. Stieglitz and by H. Goldschmidt showed that addition products must be assumed to be present in the reaction mixtures, but the exact nature of these products could not be determined.

From what has been said of the mechanism of reactions so far, it may be stated that esterification from the point

of view of the addition theory may be placed in parallel with the neutralization of an acid by a base. Both reactions belong to the general type of reaction given earlier:

$$A_nMX + H_2O = A_nMH_2OX = A_nMOH + HX$$

$\longleftarrow$ I

$\longrightarrow$ II

$\longrightarrow$ III

$\longleftarrow$ IV

$\longleftarrow$ V

I. Neutralization; II. Hydration; III. Hydrolysis or dissociation; IV. Dehydration or dissociation; V. Addition.

In the formation of a salt from an acid and a base according to I, the reaction would be:

$$HA + MOH = \begin{bmatrix} MOH \\ HA \end{bmatrix} = MA + H_2O; \qquad (a)$$

and in the formation of an ester from an acid and an alcohol, the reaction would be:

$$HA + ROH = \begin{bmatrix} ROH \\ HA \end{bmatrix} = RA + H_2O. \qquad (b)$$

The presence of a third substance which is capable of forming addition compounds with the reacting components may accelerate greatly both sets of reactions. In (*a*), water serves the purpose, and acts therefore as the catalyst for this reaction; in (*b*) some other substance such as sulfuric acid or hydrogen chloride may produce a similar effect. The formulations, including the catalysts may be given as follows:

$$HA + Cat. = \begin{bmatrix} HA \\ Cat. \end{bmatrix}, \qquad ROH + Cat. = \begin{bmatrix} ROH \\ Cat. \end{bmatrix},$$

$$\begin{bmatrix} HA \\ Cat. \end{bmatrix} + \begin{bmatrix} ROH \\ Cat. \end{bmatrix} = \begin{bmatrix} HA \\ ROH \\ Cat. \end{bmatrix} = \begin{bmatrix} RA \\ Cat. \end{bmatrix} + \begin{bmatrix} HOH \\ Cat. \end{bmatrix}.$$

$$RA + Cat. \qquad H_2O + Cat.$$

For the particular reactions in question, these would become: For (*a*)

$$HA + H_2O = \begin{bmatrix} HA \\ HOH \end{bmatrix}, \qquad MOH + H_2O = \begin{bmatrix} MOH \\ HOH \end{bmatrix},$$

$$\begin{bmatrix} HA \\ HOH \end{bmatrix} + \begin{bmatrix} MOH \\ HOH \end{bmatrix} = \begin{bmatrix} HA \\ MOH \\ 2HOH \end{bmatrix} = \begin{bmatrix} H_2O \\ MA \end{bmatrix} + 2H_2O = MA + H_2O$$

(dehydration, if MA is insoluble, etc.).

For (*b*)

$$HA + HCl = \begin{bmatrix} HA \\ HCl \end{bmatrix}, \qquad ROH + HCl = \begin{bmatrix} ROH \\ HCl \end{bmatrix},$$

$$\begin{bmatrix} HA \\ HCl \end{bmatrix} + \begin{bmatrix} ROH \\ HCl \end{bmatrix} = \begin{bmatrix} HA \\ ROH \\ 2HCl \end{bmatrix} = \begin{bmatrix} RA \\ HCl \end{bmatrix} + \begin{bmatrix} HOH \\ HCl \end{bmatrix},$$

$$\begin{bmatrix} RA \\ HCl \end{bmatrix} = RA + HCl, \quad \begin{bmatrix} HOH \\ HCl \end{bmatrix} + ROH = \begin{bmatrix} ROH \\ HCl \end{bmatrix} + H_2O.$$

Since the neutralization of an acid by a base takes place practically instantaneously, and since this reaction has been explained in past years as due to ions, rapid reaction has been taken to be a characteristic property of ionic reactions. Other reactions in aqueous solution have also been taken to bear out this view. It was shown previously how the addition theory explains the neutralization reaction; the same explanation applied to esterification shows the advantage of a common viewpoint for the two sets of reactions. The differences in velocities of the two may be explained as due to the difference in efficiency of the two catalysts, water and acid, which is in turn related to the formation of the intermediate addition compounds and their properties.

In the formation of esters in absolute alcohol, it has been found that salts such as zinc chloride increase the formation of esters especially when hydrogen chloride is also present. This is one of the common methods used in esterification. R. Engel (cf. Werner, p. 113) pointed out that the addition

of one molecule of hydrogen chloride to a molecule of zinc chloride caused at the same time the addition of at least two molecules of water to form the compound $ZnCl_2HCl.2H_2O$. Just as with the platinic chloride compounds with hydrogen chloride or water or both, hydrogen is found in the outer zone. Since water and alcohol are very much alike in many respects, it is possible that where absolute alcohol serves as the solvent, the salt effect of the zinc chloride is similar to the salt effect in aqueous solutions.

For the further discussion of similar reactions, the reader is referred to Chapter VI. In general, the term hydrolysis is taken to mean the decomposition of a substance by water. Since water is one of the products in the formation of esters from alcohols and acids, hydrolysis becomes the reverse reaction of esterification in this case. Therefore what has already been stated concerning esterification applies also to hydrolysis.

Since water is closely related to the alcohols, it is not surprising that in certain reactions alcohols play a part similar to that of water in hydrolysis. Thus, instead of:

$$HOH + En.HA = \begin{bmatrix} En \\ HA \\ HOH \end{bmatrix} = \begin{bmatrix} En \\ HOH \end{bmatrix} + HA,$$

the following may be written:

$$EnHOH + EnHA = \begin{bmatrix} En \\ En \\ HA \\ HOH \end{bmatrix} = \begin{bmatrix} HOH \\ En \end{bmatrix} + \begin{bmatrix} HA \\ En \end{bmatrix}$$
$$= \begin{bmatrix} En_2 \\ HOH \end{bmatrix} + HA$$

and, as examples of such reactions may be cited:

$$EtOH + EtI = EtOEt + HI,$$
$$CH_3.COOC_5H_{11} + CH_3OH = CH_3COOCH_3 + C_5H_{11}OH.$$

Among other methods used in the formation of esters may be mentioned the acylation of alcohols by means of acid

chlorides and acid anhydrides. These reactions really belong to the same type as the others, as can be seen from the following equations: (Cf. D. Konowalow, Z. physik. Chem. *1*, 67 (1887))

$$\mathrm{ACl} + \mathrm{EnHOH} = \begin{bmatrix} \mathrm{ACl} \\ \mathrm{En} \\ \mathrm{HOH} \end{bmatrix} = \begin{matrix} \mathrm{AOH.En} + \mathrm{HCl} \\ \\ \mathrm{EnHCl} + \mathrm{AOH} \end{matrix}.$$

It is evident that this is only an alcoholysis of the acid chloride, and corresponds to reaction III above. In a great many cases alkali aids in the formation of esters by this method. This corresponds to the addition of alkali to an aqueous solution of a salt to aid its hydrolysis. The latter is generally explained on the ionic basis as due to increasing the concentration of $OH^-$. It might, however, be explained equally well by the formation of the intermediate addition compound, which then dissociates into water, and the salt of the acid and alkali used. In other words, it favors the equilibrium for hydrolysis, by removing the acid as fast as it is liberated.

When acid anhydrides are used instead of acid chlorides, the acid group, OOCR, plays the same part as the halide in the acid halide. What has been said with regard to acid halides and their alcoholysis, applies also to the anhydrides and their alcoholysis.

Instead of alkali, other substances such as pyridine, quinoline, aniline, etc., may be used. In the case of these substances, experimental evidence shows that the pyridine, for example, combines with the acid halide. The simplest way of writing the reaction taking place would be:

$$\begin{bmatrix} \mathrm{En} \\ \mathrm{HOH} \end{bmatrix} + \mathrm{ACl} + \mathrm{Py} = \begin{bmatrix} \mathrm{En} \\ \mathrm{HOH} \\ \mathrm{ACl} \\ \mathrm{Py} \end{bmatrix} = \begin{bmatrix} \mathrm{En} \\ \mathrm{HOA} \end{bmatrix} + \begin{bmatrix} \mathrm{Py} \\ \mathrm{HCl} \end{bmatrix}.$$

Acid chlorides, etc., of inorganic acids also react with

alcohols to form esters of the acid or of the hydrogen halide. The reaction between alcohols and phosphorus halides are examples of this kind.

$$\begin{bmatrix}\mathrm{HOH}\\ \mathrm{PCl_3}\end{bmatrix} = \mathrm{HOPCl_2} + \mathrm{HCl}, \quad \begin{bmatrix}\mathrm{En}\\ \mathrm{HOH}\\ \mathrm{PCl_3}\end{bmatrix} = \begin{bmatrix}\mathrm{HOPCl_2}\\ \mathrm{En}\end{bmatrix} + \mathrm{HCl}$$

$$= \mathrm{HOPCl_2} + \begin{bmatrix}\mathrm{En}\\ \mathrm{HCl}\end{bmatrix},$$

$$\mathrm{PCl_5} + \mathrm{PhOH} = \mathrm{Cl_2P(OPh)_3}$$

(W. Autenrieth and A. Geyer, Ber. *41*, 146 (1908)),

$$\left.\begin{aligned}&\mathrm{ROH} + \mathrm{PCl_5} \rightarrow \mathrm{ROPCl_4} + \mathrm{HCl}\\ &\mathrm{ROPCl_4} \rightarrow \mathrm{RCl} + \mathrm{POCl_3}\end{aligned}\right\}$$

(W. Anschütz and W. O. Emory, Lieb. Ann. *253*, 120). The reaction between aluminium chloride and alcohols is similar in character, as follows:

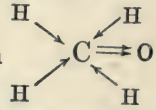
$$\mathrm{AlCl_3} + 3\mathrm{En.HOH} = \begin{bmatrix}\mathrm{AlCl_3}\\ 3\mathrm{En}\\ 3\mathrm{HOH}\end{bmatrix} = \begin{bmatrix}\mathrm{Al(OH)_3}\\ \mathrm{En_3}\end{bmatrix} + 3\mathrm{HCl};$$

etc.

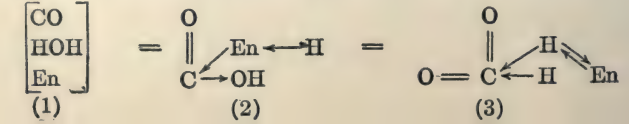
The formation of ethers may be considered from the same point of view as the formation of esters. This was indicated in connection with the reaction between ethylene and water, with sulfuric acid as catalyst, where the production of ether was shown in one of the equilibria. The reaction between alcohol and sulfuric acid to form ethyl sulfuric acid, and then, with more alcohol, ether, is also of historical interest.

The reactions between ethylene, water, and sulfuric acid, in which it was shown the products which may be formed, were given on a previous page and need not be repeated here. Ether is formed according to equilibrium (5), if the external conditions are suitable, and the substances present in suitable concentrations.

The graphic formula for ether is based mainly upon the

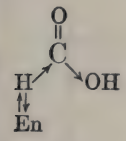
proof of the structure for alcohol as ROH. The latter rests upon the proof that one atom of hydrogen acts differently from the rest when treated with a metal like sodium, and that a hydroxyl is present, as shown by treatment with phosphorus halide. As shown in a former chapter with acids, tautomerism is possible and the alcohol may react in the form  just as acids do. Ionization is not probable for this compound, since positive hydrogen is combined with carbon predominatingly negative.

This brings up the question of the structures of organic acids, which, while not pertinent to the subject under discussion, still may be interpolated in this place. Up to this point, the acyl group in organic acids has been treated as a unit and generally indicated by the letter A. The resemblance of acyl halides to alkyl halides in their reactions with amines and alcohols, etc., the similarity between ethers and esters, and between amines and amides, points strongly to a similarity in chemical makeup or constitution. This relationship can be most simply expressed or accounted for by considering the organic acids as water which is not only olefinated, as in the case of alcohols, but as also having carbon monoxide combined with it, and thus giving them the structure $\begin{bmatrix} CO \\ HOH \\ En \end{bmatrix}$, the carbon monoxide being an unsaturated compound like water, olefin, ammonia, etc. Because of tautomeric changes within these addition compounds, just as in the hydrates and ammoniates of platinic chloride and the oxygen acids, sulfuric and nitric acids, the atoms may occupy different positions in the molecule.

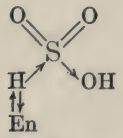


Formula (2) corresponds to the structure which is used in organic chemistry at present, the proof for which is outlined in Meyer and Jacobson's Lehrbuch der organischen Chemie ((1907) Vol. 1, p. 76) and other textbooks. The reactions cited in this proof of structure may in general be applied equally well to all three structures. The consideration of the three structures shows a closer relationship between organic acids and inorganic acids than does structure (2) alone.

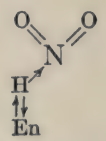
Carbon monoxide bears the same relation to formic acid that sulfur trioxide bears to sulfuric acid, or that platinic chloride bears to chlorplatinic acid, etc. Carbon monoxide also bears the same relation to the higher organic acids such as acetic, propionic, etc., acids that sulfur dioxide bears to the sulfonic acids, or that the anhydride of nitrous acid bears to the nitro compounds, etc.




Organic acid




Sulfonic acid

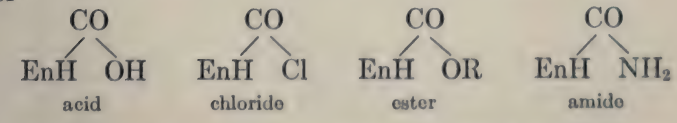



Nitro compound.

Furthermore, by the aid of these structures, it is possible to recognize the relationship between acid halides, esters, amides, and the acids themselves, more readily:

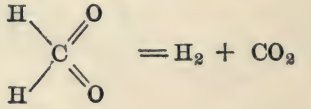
$$\begin{bmatrix} HOH \\ CO \\ En \end{bmatrix} \begin{bmatrix} HCl \\ CO \\ En \end{bmatrix} \begin{bmatrix} HOH\ En \\ CO \\ En \end{bmatrix} \begin{bmatrix} NH_3 \\ CO \\ En \end{bmatrix}$$

or



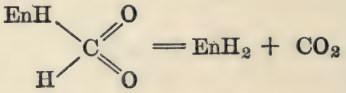

Formic acid differs from the other acids of the organic series in being simply hydrated carbon monoxide. This

structure for formic acid agrees with all the properties of the acid. It is not at all surprising that its dissociation into carbon monoxide and water is effected by catalysts such as hydrochloric acid, etc. (G. E. Branch, Jour. Amer. Chem. Soc. *37*, 2316 (1915)), since it is an addition reaction, similar to the formation of ammonium chloride from ammonia and hydrogen chloride. The explanation for the decomposition of formic acid into carbon dioxide and hydrogen is evident from formula (3) for acids given above.



This reaction involves oxidation-reduction and will therefore be discussed more fully in a later chapter. The other organic acids, such as acetic acid, etc., behave in the same way when heated with concentrated sulfuric acid, or in some cases when heated alone [W. Oechsner de Coninck, C. r. *136*, 1069 (1903)].

$$CH_3COOH = CH_4 + CO_2$$



Aromatic acids can also be included under the structures given. With them, the phenylene group plays the same part as the olefin with the aliphatic acids.

Oxalic acid would have the following structure; that of a mixed acid similar to dithionic acid.

$$\begin{bmatrix} CO \\ HOH \\ CO_2 \end{bmatrix} \text{ oxalic acid, } \begin{bmatrix} SO_2 \\ HOH \\ SO_3 \end{bmatrix} \text{ dithionic acid.}$$

This indicates the dissociation of oxalic acid into carbon monoxide and carbon dioxide, and of dithionic acid into sulfur dioxide and sulfuric acid.

If the explanation of the relation between alcohols and ethers is accepted, it becomes easier to understand alkyl compounds and their reactions in general. They fall into the same class as the ammoniates and the hydrates, and may be called olefinates. Alcohol and ether are water olefinated to different degrees. Their constitutions may be expressed as follows (Ol : olefin) : Alcohol, Ol.HOH; ether, $Ol_2$.HOH; alkyl iodide, Ol.HI; ethyl sulfuric acid, En.$H_2SO_4$; etc. The reaction for the formation of ethyl ether may be expressed as follows:

$$\text{En.HOH} + \text{Na} = \left[\begin{matrix}\text{En}\\ \text{HOH}\\ \text{Na}\end{matrix}\right] = \left[\begin{matrix}\text{En}\\ \text{HONa}\end{matrix}\right] + \text{H},$$

$$\text{En.HONa} + \text{En.HI} = \left[\begin{matrix}\text{En}_2\\ \text{HONa}\\ \text{HI}\end{matrix}\right] = \left[\begin{matrix}\text{En}_2\\ \text{HOH}\end{matrix}\right] + \text{NaI}.$$

This explanation indicates that the action of sodium upon alcohol is really the action of sodium upon water, partially olefinated. The action of ethyl iodide upon sodium ethoxide is not the replacement of the sodium by ethyl so much as the action of olefinated hydrogen iodide upon olefinated sodium hydroxide. It is the same type of reaction as the neutralization of sodium hydroxide by hydriodic acid in aqueous solution. The hydrated hydrogen iodide reacts with hydrated sodium hydroxide. The water bears the same relation to the latter reaction that the olefin does to the former.

The difference in properties of the various compoundated hydrogens can be shown by a comparison of the following compounds: ethyl iodide, ammonium iodide, and oxonium iodide. Ethyl iodide requires the highest temperature for its dissociation and the hydrate of hydrogen iodide the lowest. This shows why hydrogen is evolved if a metal is dissolved in an aqueous solution of an acid, or if a metal such

as magnesium is dissolved in a solution of an acid such as hydrogen chloride in liquid ammonia, while, if a metal like sodium or magnesium is dissolved in an ethereal solution of an alkyl halide, the olefinated hydrogen is evolved. (The ether in the Grignard reaction plays the same part as the water in an aqueous solution of the hydrated hydrogen iodide, the excess of liquid ammonia in the ammoniacal solution of the ammoniated hydrogen iodide, and if it were possible to have a solution of hydrogen iodide in liquid ethylene, containing an excess of ethylene, this ethylene would very likely act just as the solvent ether does.)

Ethers are generally spoken of as inert compounds. What is really meant is that they do not react with metals, alkalies, and most acids at ordinary temperatures with appreciable velocity. As pointed out, the properties of the olefinated hydrogen afford an explanation. The same holds true for tertiary amines. It has already been pointed out that a difference is shown in the stability, or better, the reactions of the olefinated hydrogen depending upon the other substances present. Thus, in the presence of chlorides, such as zinc chloride, etc., ethyl iodide reacts less rapidly than the chloride. The same relative order was observed with ammonium chloride, bromide, iodide, and hydroxide. The decomposition of ethers by heating with hydrogen iodide, a method used for the determination of the amount of ether groups present in compounds, may be explained on the same basis. They are simple displacement reactions. The existence of the intermediate addition compounds (oxonium salts) has been proven:

$$\mathrm{En_2.HOH + HI} = \begin{bmatrix} \mathrm{En_2} \\ \mathrm{HOH} \\ \mathrm{HI} \end{bmatrix} = \begin{bmatrix} \mathrm{En} \\ \mathrm{HOH} \end{bmatrix} + \begin{bmatrix} \mathrm{En} \\ \mathrm{HI} \end{bmatrix} = 2\begin{bmatrix} \mathrm{En} \\ \mathrm{HI} \end{bmatrix} + \mathrm{HOH.}$$

Other acids are capable of decomposing ethers. Concen-

trated sulfuric acid dissolves ether with the evolution of considerable heat, and if the mixture is heated for some time at 100 degrees, ethyl sulfuric acid and ethyl sulfate are formed. Also acid chlorides react similarly with ethers.

$$\begin{bmatrix} En_2 \\ H_2O \end{bmatrix} + ACl = \begin{bmatrix} En_2 \\ ACl \\ HOH \end{bmatrix} = \begin{bmatrix} HOA \\ En \end{bmatrix} + \begin{bmatrix} HCl \\ En \end{bmatrix}.$$

The reaction

$$2CH_3OC_5H_{11} + 2CH_3COCl \begin{cases} CH_3Cl + CH_3COOC_5H_{11} \\ C_5H_{11}Cl + CH_3COOCH_3 \end{cases}$$

may be quoted as example (F. Wedekind and J. Häussermann, Ber. *34*, 2081 (1901)).

The amines differ from the ethers and alcohols in that they are olefinated ammonia or ammoniated olefins. What has been said with regard to ethers and alcohols applies also in a general way to the amines. Primary and secondary amines correspond to the alcohols while the tertiary amines correspond to the ethers. Because of properties of the aminated compounds or ammonium salts as compared with the oxonium salts or etherates these two series of compounds as a rule are looked upon from entirely different standpoints. With the nitrogen series, the properties of the central nitrogen atom of the aminates and ammoniates predominate, while in the oxygen series the properties of the olefinated hydrogen and also of the hydrogen with the alcohols are more prominent than those of the central oxygen atom. It is only in recent years that much attention has been paid to the etherates and in general to the oxonium salts.

Because of the properties of the ammonium salts and aminates which permit of their existence under ordinary conditions, it is much easier to show the mechanism involved in the formation of amines, than in the corresponding

cases of the alcohols and the ethers. It has been possible to show the occurrence of the intermediate addition compound at ordinary temperatures with the nitrogen compounds, while with the oxygen compounds lower temperatures, and the application of the principles of the Phase Rule were necessary to prove the existence of such compounds. The formation of amines from ammonia and alkyl halides may be represented by the following equations, which differ only slightly from the way A. W. Hofmann originally expressed the reactions:

$$\mathrm{En.HX} + \mathrm{NH_3} = \begin{bmatrix} \mathrm{En} \\ \mathrm{NH_3} \\ \mathrm{HX} \end{bmatrix} = \begin{bmatrix} \mathrm{En} \\ \mathrm{NH_3} \end{bmatrix} + \mathrm{HX} \quad 1^\circ \text{ amine,}$$

$$\mathrm{En.HX} + \mathrm{En.NH_3} = \begin{bmatrix} \mathrm{En_2} \\ \mathrm{NH_3} \\ \mathrm{HX} \end{bmatrix} = \begin{bmatrix} \mathrm{En_2} \\ \mathrm{NH_3} \end{bmatrix} + \mathrm{HX} \quad 2^\circ \text{ amine,}$$

$$\mathrm{En.HX} + \mathrm{En_2NH_3} = \begin{bmatrix} \mathrm{En_3} \\ \mathrm{NH_3} \\ \mathrm{HX} \end{bmatrix} = \begin{bmatrix} \mathrm{En_3} \\ \mathrm{NH_3} \end{bmatrix} + \mathrm{HX} \quad 3^\circ \text{ amine.}$$

The acid of the alkyl halide plays the same part in the formation of amines as it does in the formation of ethers. This is emphasized in the formation of diphenylamine from aniline hydrochloride and aniline

$$\mathrm{PhNH_2.HCl} + \mathrm{NH_2Ph} = \begin{matrix} \mathrm{Ph_2NH} \\ \text{or} \\ \begin{bmatrix} \mathrm{Pen_2} \\ \mathrm{NH_3} \end{bmatrix} \end{matrix} + \begin{bmatrix} \mathrm{NH_3} \\ \mathrm{HCl} \end{bmatrix}.$$

(Pen = Phenylene)

The reason for not considering the acid of the alkyl halide to play this part in the formation of ethers, is to be found in the intermediate addition compound, the alkyl ammonium salt, which combines with the acid so that under ordinary conditions the latter is not liberated and allowed to go through the cycle again. Even in the formation of the diphenyl amine where the intermediate compound dis-

sociates, the acid is taken up by the ammonia, and thus prevented from acting as the catalyst. It will be recalled that in the chapter on catalysis it was pointed out that platinic chloride might act as the catalyst in the formation of ammonium chloride from ammonia and hydrogen chloride, if the conditions were such that the intermediate compound dissociated and liberated the platinic chloride.

Since ethers may be formed from two molecules of alcohol, and secondary and tertiary amines from two molecules of amines of lower order it should be possible to combine alcohols and amines. Such compounds have been formed by treating alcohols with ammoniated zinc chloride (V. Merz and K. Gasiorowski, Ber. *17*, 623 (1884)).

$$\begin{matrix}\text{ROH}\\ \text{or}\\ \left[\begin{matrix}\text{En}\\ \text{HOH}\end{matrix}\right]\end{matrix} + \left[\begin{matrix}\text{NH}_3\\ \text{ZnCl}_2\end{matrix}\right] = \begin{matrix}\text{RNH}_2\\ \text{or}\\ \left[\begin{matrix}\text{En}\\ \text{NH}_3\end{matrix}\right]\end{matrix} + \left[\begin{matrix}\text{H}_2\text{O}\\ \text{ZnCl}_2\end{matrix}\right].$$

H. Goldschmidt and C. Wachs (Z. physik. Chem. *24*, 353 (1897)) showed that the formation of amides (anilides) followed the same laws as the formation of esters. With both, the reaction is bimolecular in the absence of a strong acid, being autocatalyzed by the organic acid itself. The amine plays the same part in the formation of an amide as the alcohol in the formation of an ester. Instead of an oxygen ester, a nitrogen ester is formed. The same relations apply to both, and they may be formulated similarly.

$$\left[\begin{matrix}\text{En}\\ \text{HOH}\end{matrix}\right] + \text{HOA} = \left[\begin{matrix}\text{En}\\ \text{HOH}\\ \text{HOA}\end{matrix}\right] = \left[\begin{matrix}\text{En}\\ \text{HOA}\end{matrix}\right] + \text{H}_2\text{O},$$

$$\left[\begin{matrix}\text{En}\\ \text{NH}_3\end{matrix}\right] + \text{HOA} = \left[\begin{matrix}\text{En}\\ \text{HNH}_2\\ \text{AOH}\end{matrix}\right] = \left[\begin{matrix}\text{En}\\ \text{NH}_2\text{A}\end{matrix}\right] + \text{H}_2\text{O}.$$

If the catalyst is taken into account, the following equations may be given: If no strong acid is present:

$$\begin{bmatrix}\text{En}\\ \text{HOH}\end{bmatrix} + (\text{HOA})_n = \begin{bmatrix}\text{En}\\ \text{HOH}\\ (\text{HOA})_n\end{bmatrix} = \begin{bmatrix}\text{En}\\ \text{HOA}\end{bmatrix} + \begin{bmatrix}\text{HOH}\\ (\text{HOA})_{n-1}\end{bmatrix},$$

$$\begin{bmatrix}\text{En}\\ \text{NH}_3\end{bmatrix} + (\text{HOA})_n = \begin{bmatrix}\text{En}\\ \text{NH}_3\\ (\text{HOA})_n\end{bmatrix} = \begin{bmatrix}\text{En}\\ \text{H}_2\text{NA}\end{bmatrix} + \begin{bmatrix}\text{HOH}\\ (\text{HOA})_{n-1}\end{bmatrix}.$$

With an acid HX present:

$$\begin{bmatrix}\text{En}\\ \text{HOH}\end{bmatrix} + \begin{bmatrix}\text{HOA}\\ \text{HX}\end{bmatrix} = \begin{bmatrix}\text{En}\\ \text{HOH}\\ \text{HOA}\\ \text{HX}\end{bmatrix} = \begin{bmatrix}\text{En}\\ \text{HOA}\end{bmatrix} + \begin{bmatrix}\text{HOH}\\ \text{HX}\end{bmatrix}$$

$$= \begin{bmatrix}\text{En}\\ \text{HOA}\\ \text{HX}\end{bmatrix} + \begin{bmatrix}\text{HOH}\\ \text{HOA}\end{bmatrix}$$

$$\begin{bmatrix}\text{En}\\ \text{HOA}\end{bmatrix} + \text{HX}$$

$$\begin{bmatrix}\text{En}\\ \text{HNH}_2\end{bmatrix} + \begin{bmatrix}\text{HOA}\\ \text{HX}\end{bmatrix} = \begin{bmatrix}\text{En}\\ \text{HNH}_2\\ \text{HOA}\\ \text{HX}\end{bmatrix} = \begin{bmatrix}\text{En}\\ \text{H}_2\text{NA}\end{bmatrix} + \begin{bmatrix}\text{HOH}\\ \text{HX}\end{bmatrix}.$$

Amides may also be formed by other methods similar to the methods used for the acylation of alcohols, that is, with acyl halides and acid anhydrides:

$$\begin{bmatrix}\text{En}\\ \text{NH}_3\end{bmatrix} + \text{ACl} = \begin{bmatrix}\text{En}\\ \text{HNH}_2\\ \text{ACl}\end{bmatrix} = \begin{bmatrix}\text{En}\\ \text{ANH}_2\end{bmatrix} + \text{HCl},$$

$$\begin{bmatrix}\text{En}\\ \text{NH}_3\end{bmatrix} + \text{A(OA)} = \begin{bmatrix}\text{En}\\ \text{A(OA)}\\ \text{NH}_3\end{bmatrix} = \begin{bmatrix}\text{En}\\ \text{ANH}_2\end{bmatrix} + \text{HOA}.$$

The formation of amides from ammonium salts of oxygen acids is in fact only a part of the dissociation of the intermediate addition compound in amide formation from an amine and an acid. The formation of amide from ester and ammonia is similar to the formation of amide from

amine and acid except for the olefinated acid in place of the acid:

$$\begin{bmatrix} \text{En} \\ \text{AOH} \\ \text{HNH}_2 \end{bmatrix} \rightleftharpoons \begin{bmatrix} \text{En} \\ \text{HOH} \end{bmatrix} + \text{ANH}_2$$

$$\begin{bmatrix} \text{En} \\ \text{AOH} \\ \text{HNH}_2 \end{bmatrix} = \text{HOH} + \begin{bmatrix} \text{En} \\ \text{ANH}_2 \end{bmatrix}$$

$$\begin{bmatrix} \text{En} \\ \text{AOH} \\ \text{HNH}_2 \end{bmatrix} \rightleftharpoons \begin{bmatrix} \text{En} \\ \text{NH}_3 \end{bmatrix} + \text{AOH}$$

Amides may be hydrolyzed and saponified just as esters. This is only the reverse reaction to their formation. Just as with the esters, amides may also undergo alcoholysis. The reactions are as follows:

$$\text{ANH}_2 + \begin{bmatrix} \text{En} \\ \text{HOH} \end{bmatrix} = \begin{bmatrix} \text{En} \\ \text{ANH}_2 \\ \text{HOH} \end{bmatrix} = \text{AOH} + \begin{bmatrix} \text{En} \\ \text{NH}_3 \end{bmatrix}$$

$$= \begin{bmatrix} \text{En} \\ \text{AOH} \end{bmatrix} + \text{NH}_3$$

(Meyer and Jacobson, p. 609),

$$\begin{bmatrix} \text{En} \\ \text{HOA} \end{bmatrix} + \begin{bmatrix} \text{En}' \\ \text{HOH} \end{bmatrix} = \begin{bmatrix} \text{En} \\ \text{En}' \\ \text{HOA} \\ \text{HOH} \end{bmatrix} = \begin{bmatrix} \text{En}' \\ \text{HOA} \end{bmatrix} + \begin{bmatrix} \text{En} \\ \text{HOH} \end{bmatrix},$$

etc.

## CHAPTER IX.

### OXIDATION–REDUCTION.

In the last four chapters a number of chemical reactions were taken up and classified according to certain principles laid down in the earlier chapters. In Chapter V, the general consideration of reactions was outlined and some of the principles elaborated. Chapters VI and VII contained a classification of reactions based upon certain general types of chemical change, the actual substances taking part being subordinated to the general scheme. In Chapter VIII the point of view was shifted in that the change in composition of the substances reacting was emphasized. The various reactions, considered before from the standpoint of type of reaction were here developed from the position of the reacting substances, and as the special group of substances chosen, the chemical changes undergone by the olefins were outlined. In these four chapters, however, one important limitation was introduced. In the reactions and compounds which were taken up, none of the atoms in any of the molecules changed its state of oxidation. This limitation excluded all oxidation-reduction reactions which will be taken up in this and the following chapters.

It seems advisable first to define and describe the phenomena of oxidation and reduction from the newer chemical viewpoints, and then to apply these definitions and descriptions to a number of reactions.

The valence of an element is defined as the number of negative electrons an atom of that element loses or gains to form chemical linkings. Stated in somewhat different terms, the valence of an element may also be defined as the number of equivalents of the acidic or of the basic constituents combined with, or associated with, one formula

weight of that element. The symbolism used heretofore in this book and which applies with the first definition will be used here as well. The production of every chemical linking involves the loss of (at least) one electron by one atom and the gain of (at least) one electron by another atom. The formation of this linking will therefore involve a simultaneous oxidation of one atom and reduction of the other. Thus, starting with a neutral hydrogen atom and a neutral chlorine atom, in order to form a molecule of hydrogen chloride, the hydrogen atom loses a negative electron and acquires a positive charge, and the chlorine atom gains a negative electron and acquires a negative charge.

Some of the arguments in favor of such a polar view of valence have been given in the first chapter. The conclusions with regard to such charged atoms were not specially emphasized in the reactions described in previous chapters, but it is evident from what has been said already, that the valence of an atom or the nature of its electric charge is of paramount importance and significance in oxidation-reduction reactions. Change of valence is the significant feature of oxidation and reduction; the participation of oxygen or hydrogen as such has nothing necessarily to do with the reaction.

The actual charge or valence of an atom in combination is of importance in the reactions to be considered, and when, under certain conditions or by various treatments, the valence is changed, the mechanism of the reaction involving such a change is of interest. These questions are fundamental and will be considered in detail as occasion arises.

The experiments described in Chapter I showed that in any oxidation-reduction reaction involving electrolytes, that for every mol of an element undergoing oxidation or reduction, 96,500 coulombs of electricity or a simple

multiple of this quantity are involved. This holds true for organic substances undergoing oxidation or reduction as well as for inorganic substances, as long as the substance can be brought into solution and satisfactory electrical measurements made. (A practical method of illustrating such changes is by means of the "Chemometer" described first by W. Ostwald, Z. physik. Chem. *15*, 399 (1894).)

In the equation for the change in free energy or the chemical affinity of a reaction as stated in Chapter I,

$$A = RT \log_e \frac{C_1^{n_1} C_2^{n_2} \cdots}{C_1'^{n_1'} C_2'^{n_2'} \cdots} - RT \log_e K,$$

if the electromotive force of a galvanic cell in which the current is produced by the chemical reaction is denoted by $E$, and one gram equivalent of the substance in question is transformed, then

$$E = A,$$

under similar conditions of reversibility, etc., under which $A$ may be measured, using suitable units. W. Nernst developed the osmotic theory of current production, showing the mechanism by which the chemical reactions produced the electric current. Thus, the difference in potential of two solutions containing univalent ions of a completely ionized electrolyte of concentration $n_1$ and $n_2$ with mobilities of cation and anion equal to $u$ and $v$ (motion under a definite potential gradient) is given by the equation

$$E = \frac{u - v}{u + v} \cdot RT \log_e \frac{n_2}{n_1}.$$

In an analogous manner, for the solution of a metal in a solution of its salt, $E = RT \log_e P/p$ when one gram equivalent of the metal acting as electrode is dissolved, in which $P$ represents the electrolytic solution tension of the metal, and $p$ the osmotic pressure of the univalent ion

of the metal in the solution. In place of the pressures, $P$ and $p$, the corresponding concentrations, $C$ and $c$, may be used. Similar relations may be developed for negative ions and elements. A comparison of the electromotive forces developed, for example, with metals and solutions of their ions will show the relative oxidizing or reducing potentials of these elements; that is, the chemical affinities with which these elements enter into chemical combination. As pointed out before, an element entering into chemical combination forms definite chemical linkings, that is to say, gains or loses electrons. These electromotive force values are fundamental therefore for studying the chemical affinities of the simplest reactions. The theoretical and experimental developments of W. Nernst have made possible the quantitative study of the phenomena postulated by J. Berzelius more or less definitely in his electrochemical theory. N. T. M. Wilsmore (Z. physik. Chem. *35*, 291 (1900)) calculated from the best data available the relative electromotive forces shown by a number of elements as electrodes against solutions containing normal concentrations of their ions. These are known as the decomposition potentials and are based upon the value of hydrogen as zero. These values can be used to determine the replacement of metals, etc., by each other, the electromotive forces of galvanic combinations, etc. They apply directly to the concentrations indicated. For other concentrations somewhat different values must be used.

The quantitative theory of electromotive force production and its relation to chemical combination outlined very briefly and superficially (for more exhaustive treatments the reader is referred to suitable text books on physical chemistry) may be extended to chemical phenomena in general, in the same way that the experimental measurements of valence on the basis of the ionic theory of solutions were extended and elaborated in the electron conception of

valence to include all chemical compounds. Evidently this comparison is deep-seated. Since all chemical compounds are formed by the transfer of electrons producing the linkings, the atoms are all charged electrically in these compounds. The chemical affinity may then be considered to be given by the affinity of the given atom for an electron under the conditions pertaining to that compound, or in other words by a value which might be said to correspond to electric potential in electromotive force measurements. These electric potentials are not as yet susceptible to quantitative measurement in the same way as the electromotive forces in galvanic cells, but the principle is similar and the chemical affinity of a given combination may be expressed as electromotive force or electric potential, or more in conformity with the valence views used, an electron potential. This electron potential of an atom in combination will manifestly be different in different compounds, just as the electromotive force of an element is different in different combinations of solvent, etc. The electron potential cannot be measured quantitatively at present as already stated except in isolated cases, but it can be used in a qualitative sense in a classification of reactions. Recalling the definition of oxidation and reduction, it is plain that for electron potential when used to compare different substances, may be substituted relative oxidizing and reducing potentials, or what amounts to the same thing, the affinity of the element for the electron under the given conditions.

The theoretical developments outlined apply to all chemical compounds and reactions. The next step will be to study the distribution of the valence electrons in a molecule, or the valences of the different atoms in a molecule. A clear understanding of these valences (positive or negative) is necessary for the formulation of compounds on the basis of the electron conception of valence, just as fifty years ago the arrangement of atoms in a molecule and their

linkings formed one of the outstanding problems in chemistry. The reactions of the various substances preferably with simple reagents at that time formed the basis for the elucidation of the structures, the valences of the atoms then forming the general underlying groundwork for further developments. The combined study of the valences and the reactions together with the underlying principles resulted in the great growth of structural chemistry.

The same general method must now be used in the newer developments of chemical structures involving the electron conception of valence. On the basis of previous knowledge and some fundamental assumptions (as few as possible) definite rules of electron linkings may be developed. These will then be used in connection with certain simple chemical reactions, and the structures modified when necessary. In this way by correlating the relations found by these methods, certain rules for indicating structures will be developed and then applied to classifying reactions. The knowledge of the exact distribution of the valence electrons was not absolutely essential to the reactions discussed in the preceding chapters as long as there was no change in this distribution involving oxidation and reduction. Since oxidation and reduction reactions involve the change in electric charge of certain atoms, a knowledge, as complete as possible under the conditions, of the initial states of oxidation of the atoms reacting, is essential. The remainder of this chapter will be devoted to a review of some of the principles of use in the determination of the electron structures, and in the following chapter will be presented a number of oxidation-reduction reactions using the structures developed.

In the first chapter, some of the fundamental principles upon which the electronic structures of compounds may be based were outlined. Thus, the older ideas of positive and negative atoms and groups were shown to have attained

a definite and precise meaning with the electron conception of valence. The experimental determinations of transference numbers and conductances of ionized substances were shown to be a direct method for finding some of the charges on some of the atoms or groups. The arrangement of the elements in the Periodic System of Mendeléeff is, in part, an expression of the differences in the properties under discussion, and probably serves as the most general method for indicating the relative oxidation potentials of the different elements under ordinary conditions. The atom of an element of high oxidizing potential would, in forming a chemical linking, receive a negative electron from an atom of an element of low oxidizing potential, or, in other words, elements of high oxidizing potentials are ordinarily negative toward elements of low oxidizing potentials. The arrangement of the elements in the Periodic System brings out regularities such as the relative positive and negative properties of the elements. In the horizontal rows, the elements of larger atomic weights are negative toward those of smaller, receive electrons to form chemical linkings, possess higher oxidation potentials; in the vertical rows, the elements of smaller atomic weights receive negative electrons from those of larger atomic weights in forming chemical linkings.

These regularities apply however only to the stable forms of chemical linkings. It is readily conceivable that under special conditions compounds will be formed in which the linking is less stable and in which the negative electron is transferred in the direction opposite to that of the stable linking. This would be the case with elements whose oxidation potentials, or affinity for negative electrons, do not differ widely, or with elements with great inertia whose velocity of reaction is slow so that they would exist for a measurable time in unstable forms of combination. These questions will be taken up again.

In order to determine the structural formulas of substances, physical or chemical methods or both simultaneously may be used. The use of a physical method will now be given in some detail. The linking of carbon with carbon, in which partly owing to inertia to reaction, the states of oxidation of the carbon atoms cannot be determined readily, is involved in these structures (cf. K. G. Falk, Jour. Amer. Chem. Soc. *33*, 1140 (1911)).

The structures of organic acids as deduced from their ionization constants in aqueous solutions will be developed. The ionization constants ($K \times 10^5$) of the acids as calculated from the Ostwald dilution law,

$$K = \frac{\gamma^2}{v(1 - \gamma)},$$

in which $v$ = the volume in cubic centimeters containing one mol of the acid, and $\gamma$ = the degree of ionization found from the conductance ratio, will be used. Only those acids will be considered for which a fairly reliable value of $K$ has been obtained. This eliminates the highly ionized acids for which $K$ varies with change in concentration. The data refer to 25°.

In considering the structures of the organic acids, it is evident that the $\alpha$-carbon atom (the one combined directly with the carboxyl group) influences the ionization constant of the acid to the greatest extent. A classification of the acids will be given which depends upon the direction of the valences by which this $\alpha$-carbon atom is combined with the other atoms in the molecule, or its valence, or its oxidation potential. This divides the acids into four general classes which may be formulated as follows:

$$\text{I } \rightleftarrows\!\!\rightarrow C.CO_2H;\ \text{II } \rightleftarrows C.CO_2H;\ \text{III } \leftrightarrows C.CO_2H;\ \text{IV } \leftrightarrows C.CO_2H.$$

The carboxyl group is assumed to be negative to the $\alpha$-carbon atom and to exert practically the same effect on the

valence throughout. The acids belonging to class I are those in which three electropositive groups are combined with the $\alpha$-carbon atom; those belonging to class II, two electropositive and one electronegative; to class III, one electropositive and two electronegative. The ionization constants are found to increase in the order of the classes I, II, III, IV. The acids represented by formula IV, such as trichloracetic acid, are too highly ionized to give satisfactory dissociation constants, and will not be considered here.

This method of consideration differs from the ordinary one, which attributes the variation of the ionization constant directly to the nature of the neighboring atoms or groups, in assuming that the influences determining the magnitude of the ionization constant are the positions of the electric charges on the atoms. These positions indeed are determined by the nature of the adjacent atoms or groups, so that the new view is to be regarded as a development of the older idea, which serves to give it greater definiteness. The influences exerted by the double or triple bond, according to the newer point of view, are made up additively of the influences exerted by the two or three single bonds or valences. The groups combined with the $\beta$-carbon atom, or the directions of the valences of this atom, doubtless influence the ionization constant; but as will be seen, this influence is in most cases of small importance when compared with the influence exerted by the bonds of the $\alpha$-carbon atom. The groups combined in the $\gamma$, $\partial$, etc., positions doubtless exert an influence on the constants also, but this influence is negligible in the consideration of this classification.

Although the classification depends primarily upon the directions of the valences, the specific effect of certain groupings may be great enough at times to exert a predominating influence and obscure the relations mentioned.

These effects, which are unquestionably present with every atom or group in an acid, are too small to be perceived with the present methods of experiment and calculation and therefore do not interfere when the acids are divided into the general classes depending upon the directions of the valences of the $\alpha$-carbon atom except, possibly, in individual cases. Acids which contain an amino group will not be included in the discussion, and all acids containing sulfur will be omitted as well.

*Saturated Monobasic Acids.*—In the aliphatic acids containing only carbon and hydrogen in combination with the carboxyl group, the arrangement of the bonds of the $\alpha$-carbon atom may as stated be represented by the formula $\rightrightarrows C.CO_2H$. The values of the ionization constant for these acids vary between 0.0011 and 0.0020 and include the following, arranged in the order of increasing values for the constant: pelargonic, caprylic, caproic, isobutyric, heptylic, isocaproic, butyric, valeric, ethylmethylacetic, isovaleric, acetic, tetramethylenecarboxylic, and diethylacetic. The following acids and their dissociation constants contain the same bonds for the $\alpha$-carbon atom as the acids just considered, but are substituted by halogens, hydroxyl groups, phenyl groups, etc., in the $\beta$-, $\gamma$-, or $\partial$-positions: $\partial$-chlorvaleric, 0.0020; benzoylpropionic, 0.0022; hydrocinnamic, 0.0023; levulinic, 0.0026; $\beta$-hydroxypropionic, 0.0031; $\beta$-chlorpropionic, 0.0086; $\beta$-chlorbutyric, 0.0089; $\beta$-iodbutyric, 0.0090; $\beta$-brompropionic, 0.0098; and eleven substituted $\beta$-hydroxypropionic acids, 0.0015 to 0.0045. To these may be added phenylacetic, 0.0056, and hydroatropic, 0.0043, indicating that the phenyl group as a substituent exerts an influence on the ionization constants of acids similar to that exerted by the methyl, etc., groups. The ionization constants for these acids are less than 0.005 except for the three $\beta$-halogen propionic and phenylacetic acids, and for these they are less than 0.01. The constitu-

tive effect is evident here, but is it not great enough to mask the additive influence of the bonds (as will be seen presently with the $\alpha$-halogen substituted acids). For the acids containing the grouping $\rightrightarrows C - CO_2H$, the constant may be taken in general to lie between 0.001 and 0.005 with variations due to the constitutive effect of the substituting groups up to 0.01 and possibly higher.

(The data for the acids refer to 25 degrees and were taken from the results of the following observers: W. Ostwald, Z. physik. Chem. *3*, 170, 241, 369 (1889); H. G. Bethmann, Ibid., *5*, 385 (1890); M. Berthelot, Ann. chim. phys., (6), *23*, 43 (1891); A. Crum Brown and J. Walker, Lieb. Ann., *261*, 116 (1891); J. Walker, Trans. Chem. Soc., *61*, 696 (1892); P. Walden, Z. physik. Chem., *8*, 433 (1891); *10*, 646 (1892); F. Stohmann and C. Kleber, J. prakt. Chem., *45*, 475 (1892); A. Hantzsch and A. Miolati, Z. physik. Chem., *10*, 23 (1892); E. Franke, Ibid., *16*, 482 (1895); H. Euler, Ibid., *21*, 264 (1896); B. Szyszkowski, Ibid., *22*, 173 (1897); W. A. Smith, Ibid., *25*, 194 (1898); W. A. Bone and C. H. G. Sprankling, Trans. Chem. Soc., *77*, 654 (1900); D. M. Lichty, Lieb. Ann., *319*, 369 (1901); W. A. Bone, J. J. Sudborough and C. H. G. Sprankling, Trans. Chem. Soc., *85*, 534 (1904); K. Drucker, Z. Physik. Chem., *52*, 642 (1905).)

The formula for the aliphatic acids containing a halogen or similar (negative) substituent in the $\alpha$-position may be represented by $\rightleftarrows C - CO_2H$. The acids belonging to this class which have been studied are iodacetic, 0.075; $\alpha$-brombutyric, 0.106; $\alpha$-brompropionic, 0.108; bromacetic, 0.138; $\alpha$-chlorbutyric, 0.139; $\alpha$-chlorpropionic, 0.147; chloracetic, 0.155; sulfocyanacetic, 0.265; cyanacetic, 0.370; and $\alpha$, $\beta$-dibrompropionic, 0.67. For acids of this class, the constant may be taken as lying between 0.1 and 0.4 unless modified very markedly by some constitutive influence.

Few acids containing two negative substituents in the $\alpha$-position of the formula $\overset{\leftarrow}{\underset{\rightarrow}{}}C - CO_2H$ have been studied. $\alpha$, $\alpha$-Dibrompropionic, 3.3, and dichloracetic, 5.2, are the only ones for which data were found. Acids containing three negative substituents in the $\alpha$-position are too highly ionized for the purpose in view and do not give a satisfactory constant.

The constants for the acids so far considered may be summarized as follows: For the grouping $\overset{\rightarrow}{\underset{\rightarrow}{}}C - CO_2H$, less than 0.01; for $\overset{\leftarrow}{\underset{\rightarrow}{}}C - CO_2H$, 0.1 to 0.4; for $\overset{\leftarrow}{\underset{\rightarrow}{}}C - CO_2H$, greater than 2. Individual substituents modify these values to a greater or less extent, but the differences between the three classes appear to be great enough to enable a decision to be reached as to the structure of a given acid in most cases.

A group of acids for which the constants lie between those for the acids containing the groupings $\overset{\rightarrow}{\underset{\rightarrow}{}}C - CO_2H$ and $\overset{\leftarrow}{\underset{\rightarrow}{}}C - CO_2H$ is known. This group comprises the acids diisopropylglycollic, 0.013; lactic, 0.014; glycollic, 0.015; glyceric, 0.023; ethoxyacetic, 0.023; methoxyacetic, 0.034; mandelic, 0.042; phenoxyacetic, 0.076; and benzilic, 0.092. The *OR* ($R = H$ or hydrocarbon radical) is evidently the reason why these acids occupy an intermediate position between the acids containing no negative $\alpha$-group and those containing one. This *OR* group is generally taken to have an effect similar to a negative group, and would therefore be formulated $\rightarrow OR$ in the acids. Some of the acids approach the values for acids of the class $\overset{\leftarrow}{\underset{\rightarrow}{}}C - CO_2H$, but for most of them the difference is so large that it must be assumed that either the *OR* group exerts a constitutive influence masking to a great extent the effect of the bonds or that there is some action (such as inner oxonium salt formation, similar to that taking place with amino acids) between the ether or hydroxyl oxygen

and the hydrogen or other part of the carboxyl group which decreases the values of $K$ for this group of acids as compared with the acids containing a different negative substituent in the $\alpha$-position, resulting in a constant of from 0.01 to 0.1. It may be pointed out, however, that the class to which any given acid belongs may readily be ascertained as the composition taken in connection with the dissociation constant shows the structure of the $\alpha$-carbon atom. An acid such as trichlorlactic, 0.465, must be formulated somewhat differently and probably is best represented by the structure $HO \leftarrow \overset{CCl_3}{\underset{H}{\gtrless}} C - CO_2H$, or intermediate between the $\overset{\leftarrow}{\underset{\rightarrow}{}}C - CO_2H$ and $\overset{\leftarrow}{\underset{\rightarrow}{}}C - CO_2H$ classes, just as lactic acid is intermediate between the $\overset{\rightarrow}{\underset{\rightarrow}{}}C - CO_2H$ and $\overset{\leftarrow}{\underset{\rightarrow}{}}C - CO_2H$ classes.

*Saturated Dibasic Acids.*—W. Ostwald was the first to point out that the constants obtained by his dilution law for the organic dibasic acids referred to the first hydrogen ion which was formed from the acid and that the second hydrogen ionizes only in very dilute solutions, so that it does not enter into the constant as ordinarily determined. For some acids the second hydrogen begins to ionize appreciably at a dilution of about 500 liters, but the constant as determined experimentally in the usual way is found to increase rapidly with the dilution when this occurs. A study of the constants for the dibasic acids may therefore follow the lines laid down for the monobasic acids by considering the carboxyl group containing the un-ionized hydrogen as a negative substituent.

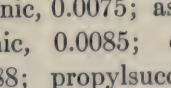
Malonic acid, from this point of view, is carboxyl acetic acid, and should belong to the $\overset{\leftarrow}{\underset{\rightarrow}{}}C - CO_2H$ class. Its constant is found to be 0.164. The following substituted malonic acids, with their ionization constants, have been measured: dimethylmalonic, 0.076; $\alpha$, $\alpha$-tetramethylenedi-

carboxylic, 0.080; isobutylmalonic, 0.090; octylmalonic, 0.095; heptylmalonic, 0.102; butylmalonic, 0.103; propylmalonic, 0.112; hexamethylenetetracarboxylic (1, 1, 3, 3), 0.12; isopropylmalonic, 0.127; ethylmalonic, 0.127; benzylmalonic, 0.151; allylmalonic, 0.154; ethylmethylmalonic, 0.164; $\beta$-benzoylisosuccinic, 0.250; methylbenzylmalonic, 0.266. These acids evidently all belong to the class $\overset{\leftarrow}{\underset{\rightarrow}{}}C - CO_2H$.

Two substituted malonic acids have been measured which doubtless belong to the $\overset{\leftarrow}{\underset{\rightarrow}{}}C - CO_2H$ class; chlormalonic, 4, and $\alpha$, $\alpha$-trimethylenedicarboxylic, 2.1.

Succinic acid may be represented by the formula

$$(\alpha)HO_2C - CH_2 \rightarrow CH_2 - CO_2H(\beta).$$

If the $\alpha$-hydrogen is ionized more easily than the $\beta$, succinic acid should belong to the $\overset{\leftarrow}{\underset{\rightarrow}{}}C - CO_2H$ class; if the $\beta$ more easily than the $\alpha$, to the $\overset{\rightarrow}{\underset{\rightarrow}{}}C - CO_2H$ class. A study of the constants for succinic acid and the acids derived from it, in which a hydrogen atom of one of the methylene groups is replaced by hydrocarbon radicals shows that the acids belong to the $\overset{\rightarrow}{\underset{\rightarrow}{}}C - CO_2H$ class (analogous to acetic acid), the negative carboxyl substituent in the $\beta$-position exerting a constitutive effect similar to that exerted by the halogens in the $\beta$-substituted propionic acids. The results for these acids are as follows: Succinic, 0.0068; isopropylsuccinic, 0.0075; asym. dimethylsuccinic, 0.0081; methylsuccinic, 0.0085; ethylsuccinic, 0.0086; isobutylsuccinic, 0.0088; propylsuccinic, 0.0089; benzylsuccinic, 0.0091; and allylsuccinic, 0.0109. The three acids, bromsuccinic 0.278, chlorsuccinic 0.284, and sym. brommethylsuccinic 0.478, evidently belong to the $\overset{\leftarrow}{\underset{\rightarrow}{}}C - CO_2H$ class analogous to chloracetic acid and must be formulated (for the first named as example)  , in which

each of the carbon atoms combined with a carboxyl has gained two and lost one negative electron.

The higher homologs of the saturated dibasic acids may be considered as derived from the higher fatty acids containing a negative substituent which exerts only a minor influence upon the ionization constants as compared with the effect of the bonds. They should therefore belong to the $\rightrightarrows C - CO_2H$ class, and, in fact, the constants for those measured are found to lie between 0.0022 and 0.0059. The following acids are included and are arranged in the order of increasing values for $K$: Camphoric, sebasic, azelaic, suberic, $\omega$, $\omega'$-dipropylpimelic, $\omega$, $\omega'$-diisopropylpimelic, *n*-pimelic, $\omega$, $\omega'$-dimethylpimelic, $\omega$, $\omega'$-diethylpimelic, adipic, glutaric, $\omega$, $\omega'$-dibenzylpimelic, $\alpha$-methylglutaric, $\alpha$, $\alpha'$-diethylglutaric, $\beta$, $\beta'$-dimethylglutaric, $\alpha$, $\alpha'$-dimethylglutaric, and $\beta$-methylglutaric.

*Unsaturated Acids.*—The unsaturated acids will be taken up in the same way as the saturated, and the double bond will be assumed to have the same effect upon the dissociation constant as if it were made up of two single bonds. It will be seen that a perfectly rational classification follows from this method of treatment and that the acids containing a double bond between two carbon atoms fall into the same groups depending upon the directions of the valences and considering their influence as purely additive, as the saturated acids. Caution must be used however with regard to the data for some of the isomeric acids, as the methods of isolating the pure substances had not been worked out very satisfactorily when some of the measurements were made. The following monobasic acids containing a double bond between the $\alpha$- and $\beta$-carbon atoms in four cases and between the $\beta$- and $\gamma$- in one case may first be quoted: Methylethylacrylic, 0.0011; sorbic, 0.0017; hydrosorbic, 0.0024; trimethylacrylic, 0.0039; and acrylic, 0.0056. These acids evidently belong to the $\rightrightarrows C - CO_2H$

class, whether the $\alpha$-carbon atom is combined with the other atoms in the molecule by means of three single bonds or one double bond and one single bond.

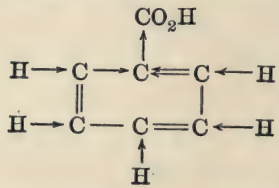
In the case of the isomeric unsaturated acids, maleic and fumaric acids may be considered in some detail, since these substances were isolated in a state of purity early and the measurements for finding the values of $K$ may be considered to be accurate. Furthermore, the composition of the two acids is simple and it should be possible to draw perfectly definite conclusions. The ionization constant of fumaric acid was found to be 0.093, and that of maleic acid 1.17. The possible structures for these acids are (*a*) $CO_2H.CH \rightleftarrows CH.CO_2H$ and (*b*) $CO_2H.CH \rightleftarrows CH.CO_2H$. Since the ionization constants refer to one hydrogen ion and the carboxyl group may be considered as a negative substituent, fumaric acid from the value of its constant should belong to the $\overset{\leftarrow}{\underset{\rightarrow}{=}}C - CO_2H$ class and must be assigned formula (*a*). Maleic acid should then be represented by formula (*b*). An acid of this formula can ionize in one of two ways, either from the $\overset{\leftarrow}{\underset{\rightarrow}{=}}C - CO_2H$ group or from the $\overset{\rightarrow}{\underset{\rightarrow}{=}}C - CO_2H$ group. The ionization constants for the acids belonging to these classes differ widely, and the value found for maleic acid, 1.17, shows that the ionization takes place by the first of the methods indicated. Maleic acid may then be classed with dichloracetic acid, and fumaric acid with monochloracetic acid in considering the ionization of the first hydrogen.

The acids containing a triple bond can be disposed of briefly, as few have been measured. Tetrolic acid, 0.246, is to be represented by the formula $CH_3\overset{\leftarrow}{\underset{\rightarrow}{=}}C.CO_2H$, and phenylpropiolic acid, 0.59, by the similar formula $C_6H_5C\overset{\leftarrow}{\underset{\rightarrow}{=}}C.CO_2H$.

*Aromatic Acids.*—The aromatic acids are taken to include those in which a carboxyl group from which the hydrogen

is ionized is in direct combination with a carbom atom of the benzene nucleus. This carbon atom corresponds to the $\alpha$-carbon atom in the saturated acids, and the bonds of this carbon atom are the ones which determine the ionization constant of the acid in question. It may be expected that a greater constitutive effect is exerted by the benzene ring on the constants. This is true to a certain extent as the general arrangement (or directions) of the valences and their influence upon each other between the carbon atoms in the ring are not known, but the aromatic acids may be grouped in the same way as the aliphatic acids and the probable reciprocal influences of the bonds discussed without specifying the particular directions of all the valences. In general terms, the benzene ring is assumed to contain alternate single and double bonds.

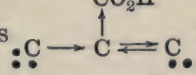
The ionization constant for benzoic acid was found to be 0.0067. This indicates that benzoic acid belongs to the $\overrightarrow{\overrightarrow{\phantom{x}}}C - CO_2H$ class, and that its graphic formula is



the direction of the bonds indicated by dashes being unknown. Other aromatic acids in which the directions of the valences for carbon (1) are the same as for benzoic acid, but for which the arrangement of the other bonds is unknown except that no strong constitutive effect is manifested by the two carbon atoms in position (2) and that therefore the directions of the bonds in these are not such as would be expected if only negative groups were combined with them, are the following: p-Hydroxybenzoic, 0.0029; vanillic, 0.0030; isovanillic, 0.0032; anisic, 0.0032; veratric, 0.0036; mesitylenic, 0.0048; m-toluic, 0.0051; p-toluic, 0.0052;

methylsalicylic, 0.0082; m-hydroxybenzoic, 0.0083; 1, 3, 5-dihydroxybenzoic, 0.0091; and p-chlorbenzoic, 0.0093.

The following acids may be assigned to the same class as benzoic acid; m-fluorbenzoic, 0.0136; m-brombenzoic, 0.0137; m-chlorbenzoic, 0.0155; m-iodbenzoic, 0.0163; m-cyanbenzoic, 0.0199; isophthalic, 0.0287; m-nitrobenzoic, 0.0345; o-toluic, 0.0120; p-nitrobenzoic, 0.0396; and 1, 2, 4-resorcylic, 0.0515. In the first seven of these acids, the negative substituent in position (3) (or corresponding to the $\gamma$-position in the aliphatic acids) apparently exerts a constitutive effect on the constant comparable with some of the effects exerted by negative constituents in the $\beta$-position of the aliphatic acids. This effect may be due to the influence of the negative constituents on the direction of the valences between the carbon atoms (2) and (3), causing the valences for (2) to assume directions, which, if present in aliphatic acids, would cause similar changes in the constants. Similar reasoning may be applied to the last three acids.

The following acids must be assigned to the $\rightleftarrows C.CO_2H$ class, and the probable structure of part of the molecule may be formulated as  : salicylic, 0.102; 1, 2, 5-hydroxysalicylic, 0.108; 1, 2, 3-hydroxysalicylic, 0.114; o-phthalic, 0.121; o-chlorbenzoic, 0.132; o-brombenzoic, 0.145; m, m-dinitrobenzoic, 0.162; and o-nitrobenzoic, 0.616.

The only acid which appears to belong to the $\rightleftarrows C.CO_2H$ class is 1, 2, 6-resorcylic, 5.0.

These results show a method for finding the directions of the valences or the distribution of some of the valence electrons on the carbon atoms of the benzene ring, and the possibilities of rearrangement of these electrons when different groups are substituted for the hydrogens of the benzene.

Chemical methods can also be used to determine the distribution of the charges in a molecule, or the valence of the atoms and should prove of more general applicability. Although no one reaction can be chosen as an infallible guide, the reaction which can be relied upon most frequently is that involving hydrolysis (cf. T. Selivanow, Ber. *25*, 3617 (1892); W. A. Noyes, Jour. Chem. Amer. Soc. *35*, 769 (1913); etc.). In this reaction, when an atom or group is replaced by a hydrogen atom or hydroxyl group derived from water, unless there is very distinct evidence to the contrary, it may be assumed that no change in the electrical states of the atoms taking part in the reaction occurs. If acid or base is present and accelerates the hydrolysis, there may be a greater possibility of electrical change, but still unless there is evidence to the contrary, no change may also be assumed here. With substances containing single bonds only, the oxidation potentials of the atoms should as a rule be so different that only one form of the substance is stable.

With compounds containing a double bond, the conditions are not so simple, however. It is necessary to consider all the possible cases and from a study of the reactions decide which formula may be assigned to a given compound. Taking up substances which contain a double bond between two carbon atoms first, it is evident that these compounds may in general be divided into classes: (1) compounds in which the two halves of the molecule are similar; and (2) compounds in which the two halves of the molecule are dissimilar. To the first class belong substances of the types

$$CR_2 \rightleftarrows CR_2;\ CR_2 \rightleftarrows CR_2;\ CRR' \rightleftarrows CRR';\ CRR' \rightleftarrows CRR'.$$

If two isomers exist in any case, because of the difference in valence of the carbon atoms or their oxidation potentials, one would be expected to be more stable than the other; if only one substance of the general type exists, then it may

be that the other is too unstable to be formed permanently, going over into the stable form, and it would be a question then to determine by means of the chemical reactions, to which of the two types its reactions show it to conform best.

Of substances derived from the formula $CR_2 : CR_2$, none is known to exist in two forms. The directions of the valences, or the charges of the atoms in the compounds of this group might be determined by following some of the addition reactions of closely related compounds. Since the molecule is symmetrical, it makes no difference in the resulting compound, in which way another substance, HI for instance, is added. If however, as a typical example, propylene $CH_3.CH : CH_2$, is taken, there would be three possibilities; $MeCH \rightleftarrows CH_2$ and $MeCH \rightleftarrows CH_2$ or $MeCH \rightleftarrows CH_2$. On treatment with HI, if either of the last two represents the structural formula, the I would all go to one carbon atom, and the H to the other, only one substance being formed; while if the first represents the structure, a mixture of two substances should be formed, the H and I being divided between the two carbon atoms. The reactions in this case might be represented as follows:

$$\begin{aligned} MeCH \rightleftarrows CH_2 &= MeCH_2 \rightarrow CH_2I \text{ and} \\ H &\rightarrow I \\ I &\leftarrow H \\ MeCH \rightleftarrows CH_2 &= MeCHI \leftarrow CH_3. \end{aligned}$$

The extent to which each of the products would be formed would depend upon the influence of the methyl group as compared with the hydrogen or the double bond, and upon the difference in polarity between the hydrogen and iodine; the smaller the difference the more nearly equal would be the amounts of the two products formed. The following results were obtained by A. Michael (J. pr. Chem. *60*, 286, 409 (1899)):

Propylene + HI formed principally $(CH_3)_2CHI$ together with a little $C_2H_5CH_2I$.

Propylene + ClBr yielded 5 parts $CH_3.CHBr.CH_2Cl$ to 7 parts $CH_3.CHCl.CH_2Br$.

Propylene + ClI yielded 1 part $CH_3.CHI.CH_2Cl$ to 4 parts $CH_3.CHCl.CH_2I$.

Propylene + HOCl formed principally $CH_3.CHOH.CH_2Cl$ and perhaps a little $CH_3.CHCl.CH_2OH$.

These examples indicate that the compounds belong to the $CR_2{\rightleftarrows}CR_2$ type, although propylene does not belong to this symmetrical type. In general, therefore, if one form exists, this formula is assigned to it, if two forms, the more stable possesses this formula.

Of substances derived from the structure CRR′ : CRR′ a large number of isomers are known, of which maleic and fumaric acids may serve as examples. From what has been said, the more stable, fumaric acid, may be assigned the formula $CRR'{\rightleftarrows}CRR'$, the less stable, maleic acid, the formula $CRR'{\rightleftarrows}CRR'$. These structures agree with the structures developed from the ionization constants of acids.

With substances containing a double bond in which the two halves of the molecule are dissimilar, there are a greater number of possibilities with three possible isomers in each case. The three isomers are not known for any one substance with certainty. The reason for this may be found in the fact that if the two halves of the molecule are made up of groups differing very much in properties, of the two isomers in which the two valences act in the same direction, one will exhibit very much greater stability than the other, making it extremely difficult, if not impossible, to isolate the less stable form. With compounds containing a double bond between two unlike atoms, the carbonyl group : CO,

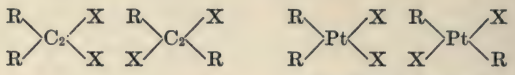
for example, the valences assigned may be indicated as $:C \rightleftarrows O$, since the properties of the two atoms differ so widely.

It must be pointed out that, although very good reasons exist for assigning the structures indicated to the various compounds on the basis of chemical reactions, the possibility remains that the reagent added may itself cause or influence the oxidation potentials of the reacting atoms, so that the structures assigned may be due primarily to the reagent used, and secondarily to the structure actually present initially. Although this possibility does not appear to apply in the great majority of cases, it must be pointed out here, as unquestionably it does occur at times.

H. S. Fry, some years ago (Z. physik. Chem. *76*, 387 (1911); cf. also L. W. Jones, Jour. Amer. Chem. Soc. *36*, 1268 (1914); K. G. Falk and J. M. Nelson, Science, *46*, 551 (1917)), denoted by the term *electromerism* the phenomenon of electronic tautomerism, including substances structurally identical, but mutually transformable by an exchange of negative electrons between the atoms composing the molecules. Thus, ammonium nitrate, $NH_4NO_3$, and hydroxylamine nitrite $NH_3OHNO_2$, while mutually transformable by a suitable exchange of negative electrons, since as far as the charges on the atoms are concerned they differ only in the valence or state of oxidation of the nitrate and nitrite nitrogen atoms, are not structurally identical and would not, therefore, be classed as electromers. L. W. Jones applied the electromerism view to a number of compounds of nitrogen in several papers published recently.

The conception of electromerism involves the isomerism of maleic and fumaric acids, and in fact all isomerism heretofore classed under cis-trans or geometrical isomerism, without considering spatial relationships at all. Another group of substances may also be included under electromerism. Werner has placed in parallel the so-called

geometrical isomerism of double bonded carbon atoms and the isomerism due to plane configuration of certain cobalt, chromium, and platinum compounds:




$(Pt(NH_3)_2Cl_2$, etc.)

Whatever explanation is accepted for the double bond isomerism, the same explanation will apply to the isomerism of the platinum compounds. Werner considers that the explanation of the spatial configuration applies to both. On the other hand, if the double bond isomerism is due to the directions of the valences, or the states of oxidation of the atoms, or the distribution of the negative electrons, then the explanation of the isomerism of the platinum compounds should be based upon the distribution of the electrons in the platinum atom. There is, however, only one atom involved here, so that it appears as if this isomerism would furnish a method for showing the distribution or arrangement of some of the electrons in an atom. These platinum and similar compounds would then belong to the class of electromeric substances. Since this explanation means that the spatial arrangements of atoms or groups around a central atom depend primarily upon the spatial arrangement of the valence and also other electrons of that central atom, a further logical deduction would include all optically active isomers in organic and inorganic chemistry in the group of electromers. The spatial arrangements of of the atoms or groups here would also be governed or controlled primarily by the arrangement of the electrons of the atom showing the optical activity.

In developing the structures of the acids, it was shown that the arrangements of the valence directions in the benzene nucleus were different in different acids, or, in other words, that the substituting group influenced the

valence electrons of the carbon atoms of the benzene nucleus. The states of oxidation of these atoms were different depending upon the substituting group. The benzene nucleus, therefore, in different compounds containing various substituents acts as an electromeric substance, and a number of reactions of benzene derivatives will undoubtedly be explained upon some such basis.

Considering the states of oxidation of the carbon atoms of the benzene ring as changed and basing explanations of reactions upon them seems more logical than the procedure of H. S. Fry, who more or less arbitrarily considers hydrogen and chlorine to be either positive or negative when combined with the benzene nucleus, and then bases explanations of substituting and other reactions upon these. While the explanations of Fry and of those using the different charges on the hydrogen atoms may for the case of benzene amount to the same thing and one view be no more advantageous than the other, in studying chemical reactions in general and building up a logical consistent system of chemical theory, it seems better to treat of the hydrogen combined with carbon as positive until direct evidence to the contrary is at hand, and to assign the changes in charges in benzene derivatives to the carbon atoms.

# CHAPTER X.

## SOME OXIDATION-REDUCTION REACTIONS.

The structures which have been developed in the last chapter with special reference to the states of oxidation of various atoms in molecules will now be applied to a number of reactions. As in the other classifications given in this book, emphasis is placed on the fact that the same principles apply to both organic and inorganic reactions and that any reaction in one branch of chemistry can be paralleled by a reaction in the other branch. In oxidation-reduction reactions, certain simple principles may first be pointed out. In these reactions, when an oxidation takes place, it is always a particular atom which is oxidized. It is incorrect to speak of a group or a molecule being oxidized, the change actually taking place with one atom in the group or molecule whose reactions are being followed and perhaps for this reason giving the impression that the group of which it forms a part is being oxidized. The same is, of course, true for reduction. It is permissible to speak of a group as predominatingly positive or negative, but if the predominating charge changes, it is because of the changes in the charges of one or more of the atoms making up the group. If oxidation takes place in a reaction in the sense that a given atom loses one or more negative electrons, then it is necessary that some other atom in one of the molecules taking part in the reaction must be reduced (gain one or more negative electrons) to a corresponding extent.

A simple reaction which may be mentioned first is that in which a metal replaces another one combined as a salt. For example, if metallic sodium is fused with magnesium chloride, metallic magnesium and sodium chloride are

formed according to the equation

$$2Na + \overset{++}{M}g\bar{C}l_2 = Mg + 2\overset{+}{N}a\bar{C}l.$$

Such reactions are common in inorganic chemistry and serve for the preparation both on a laboratory and on an industrial scale of a number of metals. If this reaction takes place in solution, as for example when zinc is immersed in a solution of copper sulfate, forming zinc sulfate and copper, while the formulation of the mechanism of the reaction is not quite as simple as in the first case, the oxidation-reduction changes are the same. Such reactions also are very common, and are the source of electric currents in galvanic cells using various combinations of metals and solutions, the electromotive forces under certain conditions being a measure of the affinity of the chemical reaction taking place.

These simple and well-known reactions of inorganic chemistry are paralleled in organic chemistry by the Würtz and Fittig syntheses and the Barbier-Grignard reaction. The Würtz and Fittig syntheses may be formulated in most general terms as follows:

$$\dot{R}\bar{X} + \dot{R}'\bar{Y} + 2\overset{\circ}{Me} = \bar{R}\dot{R}' + \dot{M}e\bar{X} + \dot{M}e\bar{Y}, \qquad (1)$$

in which $R$ and $R'$ represent hydrocarbon radicals (aliphatic or aromatic) $X$ and $Y$ halogen atoms, and $Me$ a metal such as sodium. The symbol $\overset{\circ}{Me}$ signifies an uncharged or uncombined atom of the metal. In the Würtz synthesis, aliphatic hydrocarbon halide and sodium are used, as for example:

$$2\overset{\rightarrow}{\underset{\downarrow}{C}}H_3\bar{I} + 2\overset{\circ}{Na} = \underset{(\alpha)(\beta)}{\overset{+}{H}_3\overset{\rightarrow}{\underset{\downarrow}{C}}\overset{\rightarrow}{\underset{\downarrow}{C}}H_3} + 2\overset{+}{N}a\bar{I}. \qquad (2)$$

In this reaction the neutral sodium atoms are oxidized, at the same time that a carbon atom of one of the methyl iodide molecules is reduced two units of valence from

$-3+1=-2$ to $-4$. The analogy to the inorganic reactions outlined is evident. In the same way, the Fittig synthesis deals with an aromatic halide and an aliphatic halide, as for example:

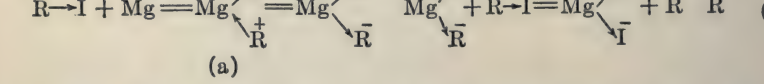
$$C_6H_5Br + C_2H_5Br + 2Na = C_6H_5C_2H_5 + 2NaBr. \quad (3)$$

The reaction is similar to the Würtz reaction, but the distribution of the valence electrons or the charges on the separate atoms are not known with the same certainty.

In these reactions, only the initial and final substances have been indicated. It is possible that the actual mechanism of the reaction is not so simple and that it takes place in several stages. Evidence for this view is to be found in an analogous reaction, in which magnesium is used in place of sodium. This reaction can be used in a great number of syntheses and is generally known as the Barbier-Grignard reaction. The ordinary formulation is as follows:

$$RI+Mg=Mg\begin{matrix}I\\R\end{matrix}; \quad Mg\begin{matrix}I\\R\end{matrix}+R'I=MgI_2+RR'. \quad (4)$$

The presence of some solvent such as ether, dimethylaniline, etc., is necessary for the reaction to proceed with measurable speed or at all. Instead of a molecule R'I taking part in the second step of the reaction, a great variety of other substances may be used and various compounds synthesized. The reader is referred to appropriate text- and laboratory books of organic chemistry for these. The formulation of equation (4) using the electron conception of valence would be as follows:



(a)

The first action consists of the combination $R^+I^-$ and atomic uncharged magnesium. The possible intermediate

product ($\alpha$) is given and may represent the first stage of combination and perhaps be equivalent to a combination such as would be produced by the force fields of Baly or some similar view as discussed in some detail in an earlier chapter. In the formation of the definite compound $\overset{++}{Mg}\begin{matrix}\nearrow I^- \\ \searrow R^-\end{matrix}$, the magnesium has been oxidized two units of valence and one of the carbon atoms of the group R reduced two units of valence. The second step of the reaction consists of a simple reaction involving ultimately an exchange without oxidation or reduction. As stated before, a number of substances may take part here. The net result is a reaction analogous to the reactions just described with the added interest that intermediate products have been isolated here which were not possible in other cases. Because of these intermediate products, it has also been possible to develop the mechanism of such reactions somewhat farther and to bring out further analogies between inorganic and organic reactions (cf. in this connection J. M. Nelson and W. V. Evans, Jour. Amer. Chem. Soc. *39*, 82 (1917)). It was stated that ether or some similar solvent was necessary for the Barbier-Grignard reaction to take place. The ether takes part in the reaction and undoubtedly forms onium (molecular) compounds with the reacting molecules. It plays the same part in these reactions that water plays in the reactions involved in galvanic cells. This is shown clearly by the following measurements of the resistances of a number of solutions:

RESISTANCE IN OHMS (ORDINARY CONDUCTIVITY APPARATUS).

| | |
|---|---|
| Ether | above $1 \times 10^7$ |
| Ether containing ethyl bromide | above $1 \times 10^7$ |
| Ether containing 1.2 gms. Mg as Grignard reagent ($MgC_2H_5Br$) per 100 c.c. | $7.1 \times 10^3$ |
| Same with 0.3 mg. Mg | $1.0 \times 10^5$ |
| 0.02 M KCl aqueous solution | $1.26 \times 10^3$ |

A cell constructed with magnesium and platinum as electrodes, and a dry ethereal solution of ethyl bromide containing a small amount of previously prepared Grignard reagent as solution, gave electromotive forces of from 0.5 to 1.5 volts.

These and similar results show that the reactions in aqueous and ethereal solutions are strictly analogous and that similar chemical forces govern all chemical reactions, organic as well as inorganic.

The reaction involving addition to a double bond between two carbon atoms was discussed very briefly in the preceding chapter. From the evidence at present available, it may be said that if the two halves of the molecule do not differ too greatly in such compounds, the linking may be represented as $:\overset{\pm}{C}\rightleftarrows\overset{\pm}{C}:$ the charges indicated being only those due to the double linking. If a halogen hydride is added to such a linking, it is not necessary to assume any oxidation or reduction reaction taking place. If, however, an element is added which in the stable form is negative to carbon, as for example chlorine, then, if the chlorine is considered to be in the state of neutral atoms, after the addition each atom will have been reduced one unit of valence, or if a chlorine molecule $\overset{+}{\mathrm{Cl}}\rightarrow\bar{\mathrm{Cl}}$ is considered to have reacted, one of the chlorine atoms will have been reduced two units of valence, while at the same time, one of the carbon atoms will have been oxidized two units of valence to give the group $\overset{\bar{\mathrm{Cl}}}{\uparrow\ddagger}\overset{\bar{\mathrm{Cl}}}{\uparrow\ddagger}$. This would be a true oxidation-reduction reaction. Similarly, if hydrogen were added to a double carbon linking, since hydrogen is normally positive toward carbon, the hydrogen would be oxidized and one of the carbon atoms reduced. These considerations refer only to the initial and final compounds of the reactions. Probably, as in the Barbier-Grignard reaction, intermediate

compounds are formed. These reactions may be illustrated by the following examples:

$$C_6H_5 - CH = CH - C_6H_5 + 2Na$$
$$= C_6H_5 - CHNa - CHNa - C_6H_5, \quad (6)$$
$$C_6H_5 - CHNa - CHNa - C_6H_5 + 2H_2O$$
$$= C_6H_5 - CH_2 - CH_2 - C_6H_5 + 2NaOH,$$

(W. Schlenk, J. Appenrodt, A. Michael, and A. Thal, Ber. *47*, 473 (1914)),

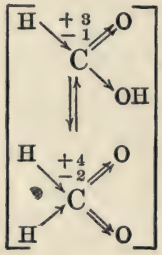
$$C_6H_5 - CH = CH - C_6H_5 + 2Br$$
$$= C_6H_5 - CHBr - CHBr - C_6H_5, \quad (7)$$
$$C_6H_5 - CHBr - CHBr - C_6H_5 + 2H_2O$$
$$= C_6H_5 - CH(OH) - CH(OH) - C_6H_5 + 2HBr.$$

The action of water here involves neither oxidation nor reduction as far as can be told and is a simple hydrolysis. On the basis of the theoretical developments, the simplest view to take is that equation (6) part 1 involves a reduction of one carbon atom two units, and equation (7) part 1 an oxidation of one carbon atom two units. The hydrolysis reactions indicate this difference also. As pointed out at the end of Chapter IX, these explanations represent the facts most nearly at the present time, but the possibility exists that the oxidation-reduction changes are actually brought about by the reagents added in the attempt to determine the structures, water in the present instance. The possibility exists and must be borne in mind even though the evidence at present available is against this explanation and in favor of the one given in greater detail.

The number of these reactions can be increased indefinitely. The addition and substitution of halogen are among the most common of the reactions in organic chemistry. As shown here and also in Chapter I in discussing polar and non-polar valence, they are actually oxidation reactions, carbon being oxidized. The reaction may be

considered to be analogous on the one hand to the transformation of ferrous chloride to ferric chloride for example, in which ferrous iron is oxidized to ferric iron and chlorine added, and on the other hand to the transformation of a compound such as phosphine to phosphorus trichloride (if this direct transformation could be carried out experimentally) in which the phosphorus is oxidized from $-3$ to $+3$. Reduction reactions may be treated similarly and need not be taken up in further detail here.

These reactions take place as a rule between two or more reacting molecules in which in the ultimate products two or more atoms have changed their valence. In a number of decomposition reactions of more or less complex substances, an intramolecular oxidation and reduction may take place, in such a manner that one atom is oxidized and another reduced at the same time that simpler molecules are formed. A simple reaction of this type is given by the decomposition of formic acid as follows:



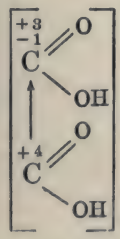

$$= H_2O + \overset{+2}{C}O \quad (a),$$

$$= H_2 + \overset{+4}{C}O_2 \quad (b). \tag{8}$$

In formic acid and its decomposition products, the directions of the valences or the charges on the atoms are fairly definitely known; as definitely perhaps as in any compound. The formula for formic acid is given in the brackets as an equilibrium between the two tautomeric forms as discussed in some detail in Chapter II. It will be noticed that in both formulas, the state of oxidation of the carbon atom is the same, $+2$. Formic acid is known to decompose in two ways; (*a*) carbon monoxide and water are formed and

(*b*) carbon dioxide and hydrogen are formed. Reaction (*a*) takes place by warming with sulfuric acid; reaction (*b*) by heating, or in the presence of finely divided rhodium, ruthenium, or iridium. It is probable that both sets of products are present to a slight extent ordinarily, but that on suitable treatment one set predominates. The products of the reaction are simple so that the states of oxidation of the various atoms in the molecules are known. It is evident therefore, that reaction (*a*) involves no oxidation or reduction of any of the atoms in the molecule, and that in reaction (*b*) the carbon atom of the formic acid is oxidized two units of valence to form carbon dioxide, and one of the hydrogen atoms reduced two units of valence to form the neutral hydrogen molecule. As stated in previous chapters, such reactions represent in reality equilibria and it may therefore be noted that the reverse of reaction (*a*) to form formic acid can be brought about with carbon monoxide and sodium hydroxide, and the reverse of reaction (*b*) with potassium or sodium amalgam, carbon dioxide, and moisture.

The decomposition of oxalic acid by sulfuric acid or heat is analogous to reaction (*a*) with formic acid:



$$= \overset{+2}{C}O + \overset{+4}{C}O_2 + H_2O \qquad (9)$$

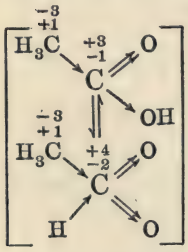
No oxidation or reduction of any of the atoms is involved in this reaction. That such reactions are not peculiar to carbon compounds is shown by the fact that the analogous sulfur compound, dithionic acid, undergoes a similar decomposition, as follows:

$$[H_2S_2O_6] = \overset{+4}{S}O_2 + \overset{+6}{S}O_3 + H_2O. \qquad (10)$$

The structural formula of dithionic acid with the charges on the atoms can be developed in the same way as with oxalic acid.

Some more complex reactions, involving hydrocarbon groups will be taken up next, but the development will follow the same lines as in the reactions just outlined together with the general principles developed. While unquestionably the reagents added influence the course a reaction takes under given conditions, these reagents are not included in the present formulations. It is intended to bring out here the possible changes in valence of certain atoms (oxidation or reduction) in fairly simple reactions, so as to lay a possible foundation for a future general classification of such oxidation-reduction reactions when a knowledge of the valence of the atoms, their charges under given conditions, and their oxidizing potentials or affinity for the negative electrons shall have been determined more precisely, especially for organic compounds, than is the case at present.

The decomposition of acetic acid may be formulated in a way similar to that of formic acid; namely as follows:



$$= \overset{-3}{\underset{+1}{H_3C}}\overset{+2}{COH} + \overset{+2}{CO} \quad (a),$$

$$= \overset{-4}{CH_4} + \overset{+4}{CO_2} \quad (b). \qquad (11)$$

The formula for acetic acid is represented as an equilibrium between the two tautomeric structures as explained in Chapter II. In both the carbon atom of the carboxyl group is in a state of oxidation of + 2. The direction of the valence between the carbon atom of the methyl group and that of the carboxyl group is given by the consid-

eration of the structures of the organic acids and their ionization constants in Chapter IX. It was shown there that malonic acid belonged to the same group of acids as chloracetic acid, only one of the carboxyl group hydrogen atoms being ionized and the other carboxyl group acting as a negative substituent. The valence of carboxyl and chlorine toward the carbon atom of the organic acid is the same, and therefore, until definite evidence to the contrary is found, in the linking between the carbon atom of the carboxyl group and that of the methyl in acetic acid, the latter is taken to give up one valence electron to the former as represented in the formula. Reaction (*a*) takes place without any of the atoms in the molecules changing valence, but in reaction (*b*) the carbon atom of the carboxyl group is oxidized two units forming carbon dioxide, and the carbon atom of the methyl group is reduced two units forming methane. As in the reactions described in Chapters VI and VII, the principle of mass action governs to a great extent the nature of the products obtained under certain given conditions. The reverse of these reactions, to form acetic acid, can be carried out; for example in reaction (*a*) with carbon monoxide and sodium methylate, in reaction (*b*), with the Barbier-Grignard reaction using carbon dioxide.

A number of reactions involving simple derivatives of acetic acid may be formulated similarly. For example, with propionyl chloride (propionyl is used instead of acetyl to illustrate the simple formation of an olefin) the reaction is formulated as follows:

$$C_2H_5 - C\begin{matrix}O\\Cl\end{matrix} = C_2H_4 + HCl + CO. \qquad (12)$$

In this reaction no oxidation or reduction has taken place. There does not appear to be the same possibility of oxidation-reduction as with acetic acid.

The reactions of an ester are as follows:

$$\left[\begin{array}{l} \overset{+3}{\underset{-1}{C_2H_5\rightarrow C}}\overset{\nearrow O}{\searrow OC_2H_5} \end{array}\right] \begin{array}{l} = \overset{+4}{C}O_2 + C_2H_6 + C_2H_4 \ (a), \\ = \overset{+2}{C}O + H_2O + 2C_2H_4 \quad (b). \end{array} \qquad (13)$$

In reaction ($a$) oxidation of the carbon of the carboxyl group has taken place, and reduction of a carbon atom of one of the hydrocarbon groups. In reaction ($b$) no oxidation or reduction of any of the atoms in the reacting molecules has taken place.

The reactions of acetoacetic ester represent a somewhat more complex case, but can be treated in the same way. Acetoacetic ester may decompose in two ways; on treatment with dilute alkali (boiling) or with dilute sulfuric acid, it undergoes the "ketonic decomposition" with the formation of a ketone, an alcohol, and carbon dioxide; treatment with concentrated alcoholic alkali results in the "acid decomposition" and formation of acid and alcohol. These transformations may be formulated as follows:

$$\left[\begin{array}{l} \overset{-3}{+1}\ \overset{-1}{+3}\ \ \overset{-3}{+1}\ \ \overset{-1}{+3} \\ H_3C\rightarrow CO\rightarrow CH_2\rightarrow C\nearrow O \\ (R) \qquad\qquad\quad \searrow OC_2H_5 \\ \qquad\qquad\qquad\quad (R_1) \\ \qquad nH_2O \end{array}\right] \begin{array}{l} = \overset{-3}{+1}\ \ \overset{-2}{+2}\ \ \overset{-3}{+1}\ \ \overset{+4}{\ } \\ \quad CH_3\rightarrow CO\leftarrow CH_3 + CO_2 + C_2H_5OH \quad (a), \\ \quad (R) \qquad\qquad\qquad (R_1) \\ = \overset{-3}{+1}\ \ \overset{-1}{+3} \qquad \overset{-3}{+1}\ \ \overset{-1}{+3} \\ \quad CH_3CO_2H + CH_3CO_2H + C_2H_5OH \ (b). \\ \quad (R) \qquad\qquad\qquad (R_1) \end{array} \qquad (14$$

Reaction ($a$) represents the ketone decomposition, reaction ($b$) the acid decomposition. $R$ and $R_1$ can be used to represent a variety of different groups. The exact relation of $R$ to the carboxyl group with which it is combined is of secondary importance, as long as it does not change in the course of the reaction. The distribution of the charges, or the valence of the atoms follows from the principles already given. In reaction ($b$), the acid decomposition, there is apparently no oxidation or reduction involved. This reaction involves the use of concentrated alcoholic alkali, a reagent which is supposed to cause or assist oxida-

tions in organic reactions. Whether it does or not, in this reaction at any rate, no oxidation appears to occur. Possibly it influences the changes occurring by removing the acetic acid as soon as formed and causing the reaction to take the indicated course (*b*) according to the principle of mass action. In reaction (*a*) on the other hand, an oxidation-reduction has occurred, analogous in every respect to the oxidation-reduction with acetic acid. The group $CH_3COCH_2$ in the former corresponds to the group $CH_3$ in the latter; in the former the product acetone corresponds to the product methane in the latter. The possibilities of tautomeric forms and intermediate products are much greater with acetoacetic ester than with the simple acids, and no attempt will be made here to formulate them.

The reaction between chloroform and alkali in which the former is hydrolyzed may be represented as follows:

$$\begin{bmatrix} \overset{+2}{\underset{-1}{H}}CCl_3 \\ 2H_2O \end{bmatrix} = \overset{+2}{\underset{-1}{H}}CO_2H + 3HCl. \qquad (15)$$

No oxidation or reduction is involved here. In order to show the uncertainties with regard to some apparently simple reactions, the decomposition of trichloracetic acid (which may take place on heating an aqueous solution) may be shown:

$$\left[ \begin{array}{l} \overset{+3}{\underset{-1}{Cl_3}}\overset{+4}{C}\leftarrow\overset{+4}{C}\overset{O}{\underset{OH}{}} \quad (a) \\ \text{or} \\ \overset{+4}{Cl_3}\overset{+3}{\underset{-1}{C}}\rightarrow\overset{+4}{C}\overset{O}{\underset{OH}{}} \quad (b) \end{array} \right] = \overset{+2}{\underset{-1}{H}}CCl_3 + \overset{+4}{C}O_2 \qquad (16)$$

The question which arises is as to the structure of trichloracetic acid; whether it is to be represented by formula (*a*)

or (*b*). The ionization constant does not give any clue, since it varies too greatly with the dilution to permit of classification. The small difference in potential between the two carbon atoms of trichloracetic acid also adds to the uncertainty as there is nothing to indicate whether one is positive or negative to the other. If formula (*a*) is correct, no oxidation or reduction is involved; if formula (*b*) is correct then the carbon atom of the carboxyl group is oxidized two units of valence and the other carbon atom reduced two units of valence in the reaction. As stated, there is no definite evidence to indicate the true nature of the reaction.

The reactions of benzenesulfonic acid have been of interest in connection with questions of valence for some time. On hydrolysis with acid, benzene and sulfuric acid are formed, with alkali, phenol and sulfite. The question of oxidation and reduction in these reactions can be approached best by considering first the structure of the benzene sulfonic acid as developed from simple principles and analogies.

In the first place, in general when carbon combines with sulfur, the carbon atom loses a negative electron to the sulfur atom. This is evident from the relative positions of these elements in the Periodic System. In the second place, in the development of the structures of the acids in Chapter IX, it was found that benzoic acid belongs to the same class as acetic acid. There is every reason to believe that in these acids, the carboxyl group as a whole is negative to the hydrocarbon group as a whole, whatever their internal structures may be, although of course the various charges are present on the individual atoms. The formation of benzoic acid from benzene and carbon dioxide might then be formulated as follows:

$$[C_6H_5]^- \leftarrow H^+ + \overset{+4}{C}O_2 = [C_6H_5]^+ \rightarrow \overset{+3}{\underset{-1}{C}}O_2H. \qquad (17)$$

A reaction of this kind might be involved in the Barbier-Grignard reaction with the formation of salicylic acid from phenol, etc., without considering the intermediate products, but only the compositions and structures of the initial and final substances. The change involves the reduction of the carbon of the carbon dioxide and the oxidation of one of the carbon atoms of the benzene. It is exactly the same change as was shown in reaction (11*b*) in the formation of methane and carbon dioxide from acetic acid which was shown to be an oxidation-reduction reaction.

The sulfonation of benzene, in which $SO_3$ plays a similar part to that of the $CO_2$ should then follow the same rules. The formulation may be indicated as follows:

$$[C_6H_5]^- \leftarrow H^+ + \overset{+6}{S}O_3 = [C_6H_5]^+ \rightarrow \overset{+5}{\underset{-1}{S}}O_2 \rightarrow OH. \quad (18)$$

Here, also, the reaction may be considered to be oxidation-reduction; the sulfur being reduced from + 6 to + 4 (+ 5 − 1), and one of the carbon atoms of the benzene ring oxidized correspondingly. This agrees, also, with the directions of the valences as deduced from the Periodic System, although too much stress must not be laid upon this point.

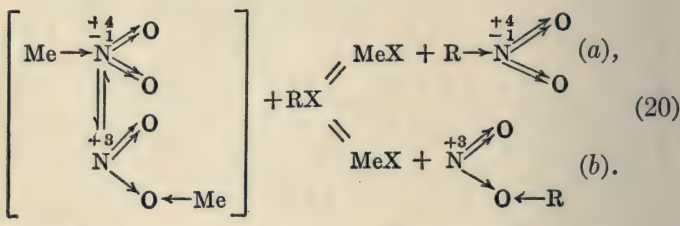
The hydrolysis reactions of benzene sulfonic acid may now be indicated, as follows:

$$\left[\begin{array}{l} C_6H_5 \searrow \overset{+5}{\underset{-1}{S}}O_2 \searrow OH \\ C_6H_5 \searrow \overset{+6}{\underset{-2}{S}}O_3 \nearrow H \end{array}\right] \begin{array}{ll} \text{(ACID)} & C_6H_5 \leftarrow H + \overset{+6}{S}O_3 \quad (b), \\ \text{(ALKALI)} & C_6H_5 \rightarrow OH + \overset{+4}{S}O_2 \quad (a). \end{array} \quad (19)$$

These decomposition reactions (the formation of sulfuric acid and of sulfite is not given in the equations but must be understood to occur) are analogous to the decomposition reactions of acetic acid, equations (11). Reactions (*a*)

in both cases involve no oxidation or reduction, reactions (*b*) are oxidation-reduction reactions. The detailed exposition with benzene sulfonic acid need not be gone into, since it follows the corresponding changes with acetic acid.

Another type of reaction may be mentioned here, which, while not oxidation-reduction, shows some of the possibilities in the way of relative oxidizing potentials of different atoms, or the relative affinities of the atoms for valence electrons. Silver nitrite and sodium nitrite when treated with an alkyl halide give different products. With the former, a nitro compound is obtained mainly; with the latter a nitrite predominates. While according to the older views, this would point to different structures for the two nitrites, according to the principles developed in this book, the explanation of these differences involves tautomerism and several chemical equilibria. The reaction may be given in general terms as follows:




(20)

The silver and sodium nitrites may exist in tautomeric forms as shown in the formula and outlined in Chapter II. There is no evidence at hand at present to show which form predominates under any given conditions. When the nitrite is treated with the alkyl halide *RX*, in all probability an addition compound is formed which is not given in the equations, and this addition compound is in equilibrium with the two sets of products represented by equations (*a*) and (*b*). There is no oxidation or reduction involved in either of these equations. Unquestionably both sets of products are obtained with any metallic nitrite. Which

product is obtained in greater amount with a given nitrite will depend upon the relative oxidizing potentials of the various atoms in the molecule. This is, in reality, only a different way of stating that the relative amounts of the two sets of products depend upon the chemical affinity or the states of the equilibria. Because of the similarity of the reactions, it would not be expected that the velocities would differ greatly, but this possibility must also be kept in mind as possibly the dominating factor in controlling the course of the reaction observed. To speak of the relative oxidizing potentials toward oxygen and nitrogen of the metal instead of the chemical affinities does not add directly to the knowledge of the reaction but brings it into line with the newer point of view developed in this book, and may aid in developing a future classification of such reactions. If the metal is sodium in reaction (20), the reaction follows course (*b*) mainly, if silver, course (*a*). It may be possible to determine the relative oxidizing potentials of sodium and silver toward oxygen and nitrogen in these reactions by suitable measurements of the equilibria under comparable conditions. This point of view may evidently be extended to a number of other reactions which show similar changes.

Finally, a classification of chemical reactions which includes all reactions in a general scheme based upon the valences and changes in the valences of the atoms in the reacting molecules may be given. In every reaction, either

I. The algebraic sum of the positive and negative charges on a definite atom of the molecules involved changes; or

II. The algebraic sum of the positive and negative charges on a definite atom of the molecules involved remains constant.

If I, the algebraic sum changes; either, *A*, the number of negative electrons on the atom in question is increased, or the number of positive charges on the atom is decreased (or reduction); or, *B*, the number of negative electrons on

the atom is decreased, or the number of positive charges on the atom is increased (oxidation).

If II, the algebraic sum remains constant; either, *A*, the arithmetical sum of the positive and negative charges on the atom in question changes; *i.e.*, the atom in question gains or loses the same number of positive and negative charges simultaneously (molecular or onium compound formation); or, *B*, the arithmetical sum of the positive and negative charges on the atom in question remains constant; *i.e.*, the electric charge on the atom in question remains unchanged.

To sum up: In every reaction—

I. If the algebraic sum of the positive and negative charges on a definite atom of the molecules changes; either, *A*, the number of negative electrons on the atoms increases; or, *B*, the number of negative electrons on the atom decreases;

II. If the algebraic sum of the positive and negative charges on the atom remains constant; either, *A*, the arithmetical sum changes; or, *B*, the arithmetical sum remains constant.

Applied to chemical reactions, I*A* includes reduction reactions, I*B* oxidation reactions, II*A* molecular or onium compound formation and decomposition, II*B* metatheses in which none of the changes I*A*, I*B*, or II*A* takes place. Stated slightly differently, the classification includes reactions involving reduction, oxidation, molecular or onium compound formation and decomposition, and simple replacement or rearrangement.

# INDEX

Authors' Names in roman, Subjects in *italics*


Abel, E., 72
Abegg, R., 98
*Acetic acid decomposition,* 158, 198, 199, 201
*Acetoacetic ester decomposition,* 200, 201
*Acetylenes,* 145, 181
Acree, S. F., 128
*Adsorption,* 69
*Aldol condensation,* 111, 115, 120, 125
*Alkyl halides,* 136–143, 145–147, 156, 160, 162, 204
*Aluminium compounds (complex),* 105, 106
*Amides,* 121, 156, 157, 163–165
*Amines,* 53, 65, 121, 142, 146, 156, 160, 161–163
*Ammoniates,* 21, 25, 26, 28, 29, 30, 31, 33, 34, 36, 38, 45, 46, 48, 57, 58, 89, 90, 136, 137, 143, 156, 159, 160, 161, 163
*"Anomalous" compounds,* 24, 25, 48, 136
Anschütz, W., 155
Appenrodt, J., 195
Armstrong, E. F., 68
Arrhenius, S., 10, 15, 41, 45, 128
Aschan, I., 105
*Atomic theory,* 1, 2, 3
Autenreith, W., 155
*"Auxiliary (secondary) valence,"* 22, 23, 24, 30, 31, 32, 37

Baeyer, A., 25, 26
Baly, E. C. C., 22, 23, 32, 67, 193
Bancroft, W. D., 72
Barbier, P., 191, 192, 193, 194, 199, 203
*Barbier-Grignard reaction,* 191, 192–194, 199, 203
Barker, T. V., 34
Baume, G., 137, 142, 150
Béhal, A., 150
*Benzene nucleus,* 182, 183, 188, 189, 203
*Benzenesulfonic acid decomposition,* 202–204
*Benzidine rearrangement,* 109, 112, 116, 122
*Benzoic acid decomposition,* 202, 203
Bernthsen, A., 129
Berthelot, M., 176
Berzelius, J., 169
Bethmann, H. G., 176
Boedtker, E., 104
Boëseken, J., 97, 98, 99
Bone, W. A., 176
Booge, J. E., 150
Bragg, W. H., vii, 34
Bragg, W. L., vii, 34
Branch, G. E. K., vi, 39, 158
Bray, W. C., vi, 39
Bredig, G., 72, 128
Brown, A., 68
Brown, H. T., 68
Brühl, J., 92
Brunel, R. F., vi
Brussow, S., 142
Buchböck, G., 56
Butleroff, A., 143

Carpenter, C. D., 27
*Chemical affinity,* 4, 5, 6, 7, 8, 14, 32, 78, 132–134, 168, 169, 170, 191, 205
*Chemical energy,* 3, 4, 5, 14
*Chemometer,* 168
Chojnacki, C., 137
*Classification of reactions,* 205, 206
Collie, J. N., 25, 26
*Color,* 105, 128
Combes, A., 103
Cone, L. H., 27
*Co-ordination number,* 31, 33, 34, 46, 47, 48, 49, 50, 51, 52, 58, 83
Crafts, J. M., 95, 103
Crehore, A. C., 34
Crum Brown, A., 176
Cullen, G. E., 68

Dakin, H. D., 68
Dawson H. M., 128
de Coninck, W. O., 158
de Forcrand, R., 137
Derick, C. G., 131, 132, 133, 134
Desgrez, A., 150
*Diazo reaction,* 116–119, 122
*Dilution law,* 53, 173, 178
*Dithionic acid decomposition,* 158, 197
*Double bond isomerism,* 180, 181, 184–186, 187, 188, 194
Drucker, K., 176
Duclaux, J., 68
Dushman, S., vi

*Electroisomers,* 15
*Electrolytic dissociation,* 10, 15, 28, 29, 35, 36, 41, 42, 45, 47, 48, 49, 52, 53, 54, 55–57, 82, 83, 86–88, 90–92, 123, 124, 125, 126, 127–130, 139, 140, 148, 152, 156, 169, 172, 173
*Electromerism,* 187, 188, 189
*Electromotive force,* 168, 169, 170, 191, 194
*Electron,* 12, 17, 167, 169, 170, 172, 183, 187, 188, 189, 190, 192, 198, 205, 206
*Electronic valence,* v, vi, 10, 11, 12, 13, 18, 24, 32, 42, 49, 54, 56, 169, 170, 171, 172, 173, 188, 192, 199, 204
Eltekoff, M., 142
Emory, W. O., 155
*Energy, capacity and intensity factors,* 3–5
Engel, R., 152
*Enzymes,* 67, 68, 69
Ephraim, F., 89, 90
*Equilibria, chemical,* 2, 6, 7, 9, 53, 54, 60, 71–75, 78, 82, 86, 88, 93, 101, 102, 108, 112, 113, 122, 129, 130, 138, 140, 144, 146, 149, 150, 197, 204, 205
*Esterification,* 63, 119, 121, 123, 125, 147, 150–154
*Etherification,* 63, 109, 110, 121, 125, 147, 155
Euler, H., 176
Evans, W. V., 127, 193

Falk, K. G., 62, 68, 127, 173, 187
Findlay, A., 26
Fischer, E., 68
Fischer, F., 105
Fittig, R., 191, 192
*Fittig synthesis,* 191, 192
*"Force fields,"* 23, 32, 37, 193
*Formic acid decomposition,* 196, 197
Franke, E., 176
Franklin, E. C., 145
*Free energy,* 4, 5, 6, 7, 8, 18, 75, 132–134, 168
Friedel, C., 25, 95, 103

*Friedel-Crafts reaction*, 64, 95–106, 108, 111, 115, 117, 120, 125, 138, 146
Fry, H. S., v, 187, 189

Gasiorowski, K., 163
Gatterman, L., 103
Genequand, P., 114
Germann, A. F. O., 137
Geyer, A., 155
Gibbons, W. A., 27
Gibbs, W., 7
Glendenning, T. A., 68
Goldschmidt, H., 128, 150, 163
Gomberg, M., 27
Grignard, V., 126, 127, 160, 191, 192, 193, 194, 199, 203
*Grignard reagent*, 126, 127, 160, 193, 194
Gulewitsch, W., 98
Gustavson, G., 96, 97, 146
Guye, P. A., 98

Hantzsch, A., 129, 176
Häussermann, J., 161
Helmholtz, H., 7
Hofmann, A. W., 53, 162
Hofmann, K. A., 26
Hohmann, C., 148, 149
Holleman, A. F., 109, 123
Hoogewerff, S., 26
*Hydrates*, 21, 26, 27, 28, 33, 36, 37 38, 45, 46, 47, 48, 49, 51, 52, 56, 57, 58, 81, 82, 83, 89, 120, 141, 147, 151, 156, 157, 159, 160

*Indicators*, 129, 130
*Ionization constant*, 53, 54, 147, 148, 173–182, 202
Isbekow, W. A., 90, 91, 92

Jacobson, P., 136, 137, 157, 165
Jones L. W., v, 187
Jones, W. J., 72

Kachler, J., 137
Kamm, O., 133
Kauffmann, H., vi
Kendall, J., 27, 105, 125, 148, 150
Kipping, F. S., 102, 103
Kleber, C., 176
Klein, D., 66
Klemensiewicz, Z., 91
Koch, J. A., 103
Kohler, E. P., 98
Kondakow, J., 136, 145, 146, 149
Konowalow, D., 145, 147, 154
Krapivin, S., 103
Kraus, C. A., 145

Lang, R., 98, 99
Langmuir, I., vi
Lapworth, A., 72, 128
Lecco, M., 24
Lercynska, I., 105
Lermontoff, J., 142
Lewis, G. N., v, vi, 39
Lichty, D. M., 176
Lieben, A., 142
Lifschitz, J., 128
Lorenz, R., 91

Maass, O., 27
McIntosh, D., 26, 27
Maihle, A., 137, 138
"*Main (principal) valence*," 31, 32
Markownikoff, W., 114
Martinsen, H., 113
Mellor, J. W., 67, 74
Mendeléeff, D., 3, 20, 172
Menschutkin, B. N., 65, 97, 98, 99 147
Menten, M. L., 68
Merz, V., 163
Meyer, V., 24, 136, 137, 157, 165
Michael, A., 195

Michael, Arthur, 138, 185
Michaelis, A., 104
Michaelis, L., 68
Millikan, R. A., 12
Miolati, A., 176
*Molecular theory*, 1, 2, 3

Nef, J. U., 99, 110, 111
Nelson, J. M., v, vi, 62, 68, 70, 127, 187, 193
Nernst W., 92, 148, 149, 168, 169
Niggeman, H., 105
*Nitration*, 108, 109, 110–115, 122
*Nitrite reactions*, 204, 205
Northrop, J. H., 70
Noyes, A. A., 130
Noyes, W. A., v, 184

*Olefinates*, 136, 137, 143, 147, 150, 156, 159, 160, 161, 165
*Onium compounds*, 27, 28, 30, 32, 38, 57, 81, 88, 89, 105, 106, 112, 193, 206
*Onium valence*, 30, 32, 37, 38, 57
Oppenheim, A., 136
*Organic acids* (*structures*), 156–158, 173–184
Ostwald, W., 53, 129, 168, 173, 176, 178
*Oxalic acid decomposition*, 158, 197
*Oxonium salts*, 25, 26, 48, 147, 159, 160, 161, 177

Pamfil, G. P., 150
Panek, C., 104
*Partial valence*, v, 133
Patten, H. E., 92
*Periodic system*, 3, 10, 13, 20, 172, 202, 203
Perrier, G., 96
Perrin, J., 3
*Phase rule diagrams*, 26, 58, 97, 98, 162
Pictet, A., 105, 114
*Platinum-ammonia compounds*, 28–31, 33, 34, 36, 38, 39, 44, 58, 188
Plotnikoff, V. A., 26, 92, 98, 103
*Polar and non-polar valence*, vi, 15, 16, 17, 19, 87, 135, 167, 195
*Potentials, oxidizing and reducing*, 13, 14, 116, 169, 170, 172, 173, 184, 187, 198, 202, 204, 205
Precht, H., 136
Prins, H. J., 103

*Reaction velocity*, 1, 6, 9, 60, 61, 62, 65, 66, 69, 70, 71, 73, 76, 79, 81, 97, 106, 108, 113, 114, 122, 123, 124, 137, 138, 142, 147, 148, 149, 152, 160, 172, 205
Rosanoff, M. A., 72
Rossi, A., 142

Sabatier, P., 64, 137, 138
Sackur, O., 91
*Salt hydrolysis*, 126
Scheffer, F. E. C., 29
Schlenk, W., 195
Schmidlin, J., 98, 99
Selivanow, T., 184
Senter, G., 128
Smith, A., 138
Smith, W. A., 176
Snethlage, H. C. S., 128
Sprankling, C. H. G., 176
Stark, J., vi
*Stereochemical capacity*, vii, 34
Stieglitz, J., v, 128, 129, 150
Stobbe, H., 26
Stohmann F., 176
Strauss, F., 26
Sudborough, J. J., 176
Sugiura, K., 68
*Sulfuric acid condensations*, 107, 111, 125, 143, 144, 145

Szyszkowski, B., 176

*Tautomerism*, 32, 38, 39, 40, 43, 44, 46, 52, 81, 82, 92, 112, 113, 117, 129, 130, 131, 147, 156, 187, 196, 198, 201, 204
Taylor, H. S., 128
Thal, A., 195
Thiele, J., v, 26, 132
Thomson, J J., v, 10, 12, 20, 92
Tickle T., 25, 26
Tissier, L., 139
Tolloczko, S., 91
*Trichloracetic acid decomposition*, 201, 202

*Unsaturation*, 23, 64, 66, 79, 92, 115, 127, 132, 135, 136, 137, 145, 180, 181

*Valence*, v, 1, 3, 4, 5, 8, 9, 10, 11, 12, 15, 17, 18, 19, 20, 21, 22, 24, 30, 32, 34, 51, 52, 57, 83, 105, 135, 166, 167, 169, 170, 171, 173, 174, 183, 184, 185, 187, 188, 191, 193, 194, 196, 197, 198, 199, 200, 202, 203, 204, 205
*Valence linkings*, 3, 9, 20, 34, 64, 167, 170, 171, 172
van Dorp, W. A., 26
van Slyke, D. D., 68
van 't Hoff, J. H., 7, 74
Varet, R., 103
Vienne, G., 103
Villiger, V., 25, 26
Vorländer, D., 26
Vosburgh, W. C., 68

Wachs, C., 163
Walden, P., 176
Walker, J., 176
Walker, J. W., 87, 99, 104
Washburn E. W., 56
Wecker, E., 105
Wedekind, F., 161
Werner, A., vi, 21, 23, 24, 28, 30, 31, 32, 34, 35, 38, 42, 44, 50, 54, 83, 90, 124, 152, 187, 188
Wieland, H., 105
Wildermann, M., 142
Willstätter, R., 114
Wilsmore, N. T. M., 169
Wroczynski, A., 98
Würtz, A., 191, 192
*Würtz synthesis*, 191, 192

*Zinc chloride condensations*, 106, 107, 125, 145, 146, 149, 150, 163
*Zones, inner and outer*, 31, 32, 35, 37, 38, 44, 45, 46, 47, 49, 50, 52, 54, 56, 57, 58, 81

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